

THE METALLIC STATE

ELECTRICAL PROPERTIES
AND THEORIES

BY

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PREFACE

THE name 'Physical Metallurgy' was suggested by Dr. W. Rosenhain, F.R.S., of the National Physical Laboratory, in order to distinguish that branch of metallurgy which deals with the structure and physical properties of metals, from the science of the extraction of the metals from their ores. To those immediately concerned, it has become increasingly apparent that Physical Metallurgy is at present in an unsatisfactory position, largely owing to the lack of collaboration which has existed between Physics, Chemistry, and Metallurgy. On the one hand the 'Practical Metallurgist' has amassed a considerable amount of information in connexion with the metals of commercial importance, but has made little or no attempt to investigate the properties of metals and alloys systematically from the point of view of the Periodic Table, in order to discover the general principles involved. On the other hand, the Physicist in his investigation of the electrical and other physical properties of metals has not merely often failed to examine these systematically from the point of view of the Periodic Table, but has also in all too many cases been out of touch with scientific metallurgy, with the result that much experimental work of the highest quality has been carried out on specimens which any scientific metallurgist would have condemned as unsuitable.

On the theoretical side, the Metallurgist has, in the past, been profoundly suspicious of the value of theoretical work, and although this attitude has changed greatly in recent times, it tends even now to discourage research work on metals which are not of possible commercial value, and this very greatly hinders the development of a connected science of Physical Metallurgy, since in many cases it is the rare or commercially unimportant metals which occupy the 'key' positions, and which are likely to provide clues to the general principles. It is only necessary to consider the position in which Chemistry would be to-day if work had been confined to commercially important elements, in order to understand the reason for the present unsatisfactory condition of Physical Metallurgy. This difference between Chemistry and Metallurgy is, of course, largely the

result of the fact that modern Chemical Industry has been developed chiefly from the scientific work of the laboratory, whereas Metallurgy has to a much greater extent grown from older traditional methods.

As regards their direct applications to the physical properties of metals, the theories of the Physicists have been concerned very largely with the electrical and thermal properties. For this reason it seemed advisable that any attempt to develop a connected theory of Physical Metallurgy should be based on a general understanding of the existing physical theories and of the data on which they were based, and the present book has been written in the hope of supplying a general survey of this kind. Examination having shown that the theoretical work has at present led to little real quantitative theory or systematization, I have adopted the policy of dividing the book into two sections, one dealing with the facts, and the other with the theories.

The first section of the book is not intended as a comprehensive treatise or text-book, but rather as a general account of those electrical and thermal properties, including Thermal Conductivity, which appear of interest from the theoretical point of view, and I have endeavoured to concentrate on subjects which are not found in the average text-book. I have, for example, omitted all reference to Specific Heats, since these are dealt with in most books on Physical Chemistry. Except for a brief reference in connexion with Contact Potentials I have also omitted Electrode Potentials and similar properties, partly because of the existence of many books on Electro-Chemistry, and also because it is increasingly apparent that these properties are greatly affected by secondary factors. I have, however, included a general survey of the Emission Phenomena, since these are so very important in connexion with the later electronic theories. In several cases, where the facts have not yet been reduced to order, I have intentionally given a very simplified and rather superficial account, in order to avoid confusing the reader with a mass of apparently unconnected facts. I have, for example, paid but little attention to the electrical properties of the ferromagnetic metals, since these are clearly abnormal, and the need at present is for a better understanding of the general principles of the normal elements. In the same way, except for the Trans-

verse Effect, I have omitted all detailed reference to the complex Galvano-magnetic and Thermo-magnetic Effects, since the work of Dr. Kapitza has shown how misleading conclusions may easily be drawn from results obtained with impure specimens at comparatively low field strengths.

As explained in the introduction to Section II, I have endeavoured to describe the theoretical work in such a way that both the general reader and the more serious student will find the information they need. Criticism may be directed at the space which has been allotted to the older theoretical work, but as the modern theories are so very much obscured by the complicated mathematics involved, I am convinced that it is easier for the average student to begin by considering the older work in some detail, than to plunge directly into the conceptions of the new methods. The inclusion of the chapter on the Intermediate Theories is also open to criticism, since these are sometimes admittedly little but discarded speculations. But apart from the desirability of some historical record, and the fact that these theories discuss points which are ignored in the modern theories on account of the drastic simplifications made in the mathematical development, I think there may be some educational value in making the student read a critical discussion of a discarded hypothesis. For, with the growth of scientific knowledge, there is an increasing danger of the student tending to absorb one fact after another without ever learning to think about them critically.

Most of this book has been written from the study of original papers, but of the books which I have found helpful I must acknowledge particularly *The Report of the Solvay Congress of 1927*, the volumes of Guertler's *Metallographie* dealing with Electrical and Thermal Conductivities of metals and alloys, O. W. Richardson's *Emission of Electricity from Hot Bodies*, H. S. Allen's *Photo-Electricity*, J. J. Thomson's *Corpuscular Theory of Matter*, and also the late H. A. Lorentz's *Theory of Electrons* (Leipzig, B. G. Teubner; New York, G. E. Stechert & Co.), from which I have kindly been allowed to reproduce the proof of the Lorentz Conductivity Equations. Much of the work has been written from notes made in libraries, and if this has in some places resulted in the reproduction of the original phrases

of authors' papers, I hope this may be excused in view of the large amount of reading involved.

I have also to acknowledge the very great help and criticism which I have received from many friends in the preparation of this book. Dr. P. Kapitza has kindly read the chapters on Electrical Conductivity, Dr. Ezer Griffiths that on Thermal Conductivity, Dr. J. L. Haughton that on Thermo-electricity, Professor O. W. Richardson that on Emission Properties, and Dr. J. A. V. Butler that on Contact Potentials. In the theoretical section I have received great help from Dr. R. H. Fowler, Professor J. E. Lennard-Jones, and Mr. I. O. Griffiths, the last-named having kindly read almost the whole manuscript in one form or another, whilst I have also to acknowledge assistance from Professor F. A. Lindemann, Dr. M. Fraser, and Dr. N. V. Sidgwick.

I have been persuaded to include a summarized translation of the paper by Dr. F. Bloch on Conductivity, in the hope that this may be of assistance to those students who may be troubled by the language (German) of the original. I have to thank Dr. Bloch and his publishers, Herren Julius Springer, for permission to do this, and must also acknowledge my indebtedness to Professor Lennard-Jones, Mr. I. O. Griffiths, and Dr. H. Bethe, without whose assistance this would never have been completed.

In connexion with the proof corrections I have to thank my father, who has gone through the proofs many times, and I must also acknowledge my gratitude to the Clarendon Press for the very great help they have given.

I need hardly say that the fact that the friends mentioned above have read the manuscript in no way commits them to the views which I have expressed, and I may add that in the preparation of this book I have been increasingly conscious of my inability to do full justice to its subject-matter.

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INTRODUCTION

IN order to describe the electrical properties of metals it is necessary to adopt some scheme of classification for the numerous metallic substances which are met with in alloy systems, and for this purpose we shall use the general method previously suggested by the present author. The development of the science of Metallography, and the study of equilibrium conditions in alloys, have led to the determination of a large number of 'equilibrium diagrams' for alloys of two or more metals. These diagrams show the limits of temperature and composition within which an alloy of several metals is homogeneous, and those in which the alloy consists of two or more phases, and in the latter case a properly determined equilibrium diagram enables us to see the compositions of the phases which are in equilibrium at different temperatures. These diagrams have been constructed chiefly by the methods of thermal and microscopic analysis, supplemented in some cases by determinations of electrical conductivity, whilst in the last few years the crystal structures of a number of alloys have been investigated by X-ray analysis.

For simplicity we may first confine our attention to solid binary alloys, and may consider what happens if we take two metals *A* and *B*, and alloy them in different proportions. In such a case we find that, in general, if we add small quantities of one metal to another, the resulting alloy remains homogeneous, with the formation of a so-called 'solid-solution'. The X-ray methods have shown that these solid solutions retain the crystal structures of the solvent elements, and fall into two main classes. In the more general 'substitutional solid-solutions', the solute atoms replace the atoms of the solvent metal upon its lattice, so that the two kinds of atoms are situated at random upon a common lattice, and we propose to call solid-solutions of this type *Primary Substitutional Solid-solutions*. In the more restricted class, of which the typical example is that of the iron-carbon alloys (steels), the solid-solution is of the interstitial type, the solute atoms fitting into the empty spaces between the atoms of the solvent, and such phases may be called *Primary Interstitial Solid-solutions*. In the case of ternary alloys the primary solid-solution may be of both types; thus in an austenitic manganese steel we have a primary substitutional solid-solution of iron and manganese forming an interstitial solid solution of carbon.

Introduction

When the equilibrium diagrams are drawn in their usual form, these primary solid solutions form the 'end phases', and their solid-solubility limits vary very greatly in the different systems. In some cases, as for example the alloys of copper with nickel, or of silver with gold, the two metals are completely miscible in the solid state, and form a continuous primary solid-solution from 100 per cent. of the first metal to 100 per cent. of the second, whilst in other systems such as the alloys of gold with lead or thallium, the mutual solubility is so slight as to be detected only with difficulty. In the more general case, the limits of the primary solid solutions vary with the temperature, and when the solubility limit is exceeded a second phase makes its appearance, and the alloys are no longer homogeneous. In such cases the simplest type of alloy is one in which the only phases met with are the primary solid-solutions, so that all intermediate alloys fall into one of three classes, a primary solid solution of *A* in *B*, a similar solid-solution of *B* in *A*, or a mixture of the two primary solid-solutions. Examples of this type are the alloys of lead with silver, antimony, or cadmium.

In the more general case, however, the intermediate alloys of two metals contain new phases with structures different from those of the parent metals, and it is in connexion with the classification of these substances that difficulty has arisen. In some alloys the two metals form one or more intermediate phases of which the compositions are fixed, or of very restricted range, and correspond to simple atomic ratios. Examples of this kind are the alloys of calcium with tin, in which there are three intermediate phases of compositions agreeing with the formulæ CaSn_3 , CaSn , and Ca_2Sn , and since these are of fixed composition, and possess properties quite distinct from those of pure metals, they are generally classed as intermetallic compounds.

But in many other alloy systems, particularly if the atomic volumes of the two metals are not very different, intermediate phases of variable composition are found. In some cases, such as the so-called ' β Brass' which ranges round the equi-atomic composition in the copper-zinc alloys, these intermediate phases, whilst differing in crystal-structure from the parent metals, appear to possess many of the properties, such as plasticity, &c., of pure metals or primary solid-solutions. But in other cases this is not so, and the intermediate phase, although of variable composition, may possess properties quite distinct from those of pure metals. The difficulty in classifying such substances lies in

the fact that the majority of the 'Text-book' definitions have failed to consider the possibility of a true compound forming a solid solution with its component elements, and the way in which such a solid solution may be distinguished from one in which no compound is formed.

From the point of view of the older atomic theory, however, the distinction was quite plain. The physical mixture of the two elements was considered as a mixture of the individual atoms or molecules, whilst in the compound the different atoms were bound together into compound molecules, and these behaved as distinct entities. For many years this conception was purely hypothetical, but the comparatively recent work on positive-ray analysis and mass spectra has led to the conclusive experimental detection of the individual molecule, the existence of which is now a fact and no longer merely a supposition. The formation of these molecules is regarded as due to the sharing or exchange of electrons between two atoms. At first sight, therefore, it might seem justifiable to define a metallic compound as one in which the constituent atoms had united to form a compound molecule, but unfortunately almost all the methods for detecting the existence of individual molecules depend upon the examination of the substance in the gaseous or liquid state, which is in general very difficult at the temperatures of molten metals. A start in direction has been made by the Japanese scientists, notably

Honda and his collaborators, by the study of the magnetic properties of molten alloys, and in this way it has been shown that some of the phases of intermediate composition found in solid alloys correspond to entities in the liquid, whilst others do not. In another connexion the work of Barratt and others on the spectra of metallic vapours has led to the observation of band spectra, which must be due to polyatomic molecules. But even in cases such as these, there is always the possibility that a true compound may be formed in the solid, but may decompose on melting or volatilization. In general, therefore, we have to examine the solid alloys alone, and here the connexion between the molecule and the crystal structure is not always clear. In many compounds, notably those met with in organic chemistry, the molecules retain their individuality in the solid crystal, but in others, such as sodium chloride, there is no sign of the individual molecule in the crystal lattice, although the high-temperature work of Nernst and others shows that, in the gaseous state, sodium chloride consists mainly of undissociated polar molecules.

We are not, however, driven to believe that sodium chloride is a compound in the gaseous state and a mixture when solid, because the work of Rubens on Reststrahlen indicates conclusively that the units in the solid crystal are not neutral atoms of sodium and chlorine, but are charged ions, each sodium atom having lost and each chlorine atom gained an electron. This is in agreement with the more refined methods of X-ray analysis. It must again be emphasized that this is now a definite experimental fact, and not merely a supposition.

From these considerations, therefore, we may next define as *Secondary Metallic Solid-solutions* those solid-solutions of intermediate composition in which the crystal structures are different from those of the parent metals, but in which there is no indication that compound molecules are formed, or that exchange of electrons is taking place, and in which electron sharing, if such occurs, is of the same nature as that existing in the normal metallic bond of pure metals, or primary solid-solutions.

Finally we may define as *Intermetallic Compounds of Fixed or Variable Composition* those intermediate phases in which there is evidence, direct or indirect, that electrons exchange or sharing is taking place, or that a compound molecule is being formed.

With the exception of the border-line cases which we shall discuss below, the above scheme gives a satisfactory fundamental distinction, although it must be admitted frankly that in many cases our experimental methods may not yet be sufficiently advanced to enable us to distinguish between secondary metallic solid-solutions and intermetallic compounds, and in such cases we must just select the more probable alternative. Where, as for example in the β brasses, we have a phase of variable composition with a crystal structure differing from those of its parent metals, but with many properties of pure metals or primary solid-solutions, we may reasonably classify it as a secondary metallic solid-solution. It has, for example, been suggested by W. Rosenhain that in cases such as those of the β brasses we have what may be considered as a solid-solution of zinc in an allotropic form of copper. In many ways this illustration is very apt, since it indicates just what it is desired to express above, namely, that although the crystal structure is different from that of both copper and zinc, the forces holding the atoms together are just the same as those in pure metals or primary solid-solutions.

On the other hand, where we have a phase of fixed or practically

fixed composition, with properties quite different from those of the parent metals, we may reasonably describe it as an inter-metallic compound, even though we have no really conclusive evidence that a compound molecule exists or that electron sharing is taking place. In such cases, as has been pointed out by J. D. Bernal, we may expect intermetallic compounds to fall into different classes. We may have, for example, what is essentially an ionic or salt-like compound in which the two kinds of atoms have exchanged electrons, and in which the metallic properties only occur because the resulting negative ion is not very stable, and so liberates electrons on account of thermal vibrations, &c. Alternatively we may have an ionic and metallic compound in which electron transference has taken place, but in which some electrons are left free to form the normal metallic kind of linkage. In the same way we may have what are essentially co-valent or homopolar compounds, i.e. compounds formed by electron sharing, in which the metallic properties only occur as the result of the liberation of electrons by the breakdown of the co-valent bonds, or alternatively we may have homopolar and metallic compounds in which some electrons are held in homopolar bonds, whilst others are left free to form the normal metallic linkage. As will be appreciated from the concluding section to this book, it is probable that, at very low temperatures, these different classes of intermetallic compounds will show characteristic temperature variations of electrical conductivity, but at present little classification has been made on these lines.

It will be noted that in the above scheme of classification we have referred repeatedly to the 'normal metallic kind of linkage', and to be complete and logical we must explain what is meant by this expression, and it is here that difficulties arise. In the crystals of some elements it is certain that the forces holding the atoms together are almost identical with the normal co-valent bonds of chemistry. The typical example of this kind is the structure of the diamond, in which each carbon atom is surrounded tetrahedrally by four neighbours, so that each atom exerts its normal valency of four, and the whole crystal is in effect one immense molecule ('Riesenmolekül'), and differs only from a compound such as carborundum, CSi , in that all the atoms are identical. As we shall see later (p. 308), there are other elements such as Silicon and Antimony, and some intermetallic compounds, which are of this type, and for which the whole crystal is to be looked upon as one single molecule in which the atoms

are bound together in the solid by simple co-valent or homopolar bonds. From the concluding chapters to this book it will be appreciated that the general tendency of the modern theories is to regard the normal metallic linkage found in pure metals as a kind of co-valent or homopolar bond which differs from that of the diamond only in the extent in which interchange between the different electrons is possible. From this point of view it may therefore be argued that we cannot really draw a hard and fast line between the metallic and co-valent type of linkage,* but that we have in effect a gradual transition from the normal metal such as sodium in which electronic interchange is quite free, to the other extreme of the diamond in which an electron is so firmly bound to two atoms that very high external potential differences are required to break down the linkage and to produce conductivity. Strictly speaking this argument must be accepted, but in the great majority of cases, especially at low temperatures, the differences in the freedom of interchange are so marked that little difficulty arises from considering the metallic bond as distinct. On the other hand, it must be recognized frankly that at higher temperatures there are elements such as Silicon which in the solid crystal are essentially co-valent structures, but in which metallic properties appear owing to the breakdown of the co-valent bonds. For the present, therefore, we shall adopt the policy of classifying metallic substances into (1) Pure Metals, (2) Primary Metallic Solid-solutions, (3) Secondary Metallic Solutions, and (4) Inter-metallic Compounds of Fixed or Variable Composition, and it must be appreciated that the last named will eventually require further sub-division not merely into ionic, ionic-metallic, homopolar (co-valent), and homopolar metallic compounds, but also so as to distinguish 'Riesenmolekül' substances analogous to elements such as Carbon (diamond) or Silicon, in which the whole solid crystal is an immense molecule even though no molecule exists in the liquid state.

* In this connexion see p. 315 for the case of Titanium, which is particularly interesting as having the normal type of metallic crystal structure, but at the same time a negative temperature coefficient of resistance at low temperatures.

THE ELECTRICAL CONDUCTIVITY OF PURE METALS AND THE FACTORS WHICH AFFECT IT

1. Specific Conductivity and Resistance of Metals—Deviation from Ohm's Law—Data for single crystals	1
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1. Specific Conductivity and Resistance of Metals

IT is not within the scope of the present book to give anything like a comprehensive account of the extensive work which has been carried out on the electrical conductivities of metallic substances, but a general understanding of the factors affecting conductivity is essential, since it is these properties which have contributed so very greatly to our understanding of the nature of metals.

The essential property of the metals is that they conduct electricity electronically, i.e. by the motions of electrons alone, without a transference of atoms or ions. Any given piece of metal offers a definite resistance to the flow of the current, and this resistance varies with the external conditions such as temperature, pressure, &c. In order to have some standard of comparison we usually deal with the *specific resistance*, which is the resistance, measured in ohms, of a piece of metal one centimetre long, and of one square centimetre cross-section; we shall denote this by the symbol W , the numerical value of which is an indication of the difficulty with which a current passes through the metal. The reciprocal of this is the *specific conductivity*, which is measured in reciprocal ohms, and which we shall denote by the symbol C .

Under all normal conditions the resistance of a piece of metal is independent of the strength of the current which is flowing through it, and it is this fact which is the basis of the well-known Ohm's Law, according to which the current strength is directly proportional to the difference of potential, and inversely proportional to the resistance. This law rests solely on an experimental basis, and its establishment is thus of great importance. From the time of the Report to the British Association by Clerk-Maxwell

The Electrical Conductivity of Pure Metals

TABLES I AND II

	Name of Metal.	Specific Resistance. $\frac{W}{l}$	Temperature Coefficient of Resistance	Pressure Coefficient of Resistance $\frac{1}{W} \frac{dW}{dp}$
		in Ohms-cm. at 20° unless otherwise stated.	0 unless otherwise stated.	at 0° C. unless otherwise stated.
	Lithium	9.3×10^{-6}	475×10^{-6}	$+ 7.72 \times 10^{-4}$
	Beryllium	10.3 "	328 "	$- 1.11$ (30° C.)
11	Sodium	4.6 "	550 "	$- 66.3 \times 10^{-4}$
12	Magnesium	4.46 "	(between 0° & m.pt.) 410×10^{-6}	$- 4.77$ "
13	Aluminium	2.62 "	467 "	$- 4.49$ "
	Silicon	85×10^3	Complex. See p. 18.	—
19	Potassium	7.0×10^{-6}	580×10^{-6}	$- 175$ "
20	Calcium	4.6 "	(between 0° & m.pt.) 364×10^{-6}	$+ 10.6$ "
22	Titanium	355 "	$- 352$ " (highly abnormal See p. 18.)	—
24	Chromium	2.6		
25	Manganese .	5.0		
26	Iron .	10.0		
27	Cobalt .	9.7	657×10^{-6}	$- 2.41 \times 10^{-6}$
28	Nickel .	6.9	658	$- 0.94$ "
29	Copper .	1.69	634	$- 1.88$ "
30	Zinc .	6.0	429	$- 2.01$ "
31	Gallium .	53	416	$- 5.4$ "
			396	$- 2.47$ "
32	Germanium .	89×10^{-3}	(0° to m.pt.)	—
33	Arsenic .	35×10^{-6}	Complex. See p. 18.	—
			389×10^{-6}	$- 3.26 \times 10^{-6}$
34	Selenium .			(impure)
37	Rubidium .	12.5	553×10^{-6}	$- 179 \times 10^{-6}$
38	Strontium .	23.0	(to m.pt.) 383×10^{-6}	$+ 50.2$ "
40	Zirconium .	170	0.004 "	$- 0.43$ "
42	Molybdenum	4.77	434 "	(at 30°) $- 1.33 \times 10^{-3}$
44	Ruthenium .	10.0	—	—
45	Rhodium		424×10^{-6}	$- 1.74$ "
46	Palladium	10.8		(at 30°)
47	Silver .	1.62	370 "	$- 1.98$
48	Cadmium	7.5	410 "	$- 3.58$
49	Indium	9.0	424 "	$- 10.6$
50	Tin .	11.4	474 "	$- 12.3$
51	Antimony	39	436 "	$- 10.4$
52	Tellurium	110-1	511 " Abnormal	—

TABLES I AND II (continued)

Atomic Number.	Name of Metal.	Specific Resistance. W in Ohms-cm. at 20° unless otherwise stated.	Temperature Coefficient of Resistance $\frac{1}{W_0} \frac{W_{100}-W_0}{100}$ unless otherwise stated.	Pressure Coefficient of Resistance $\frac{1}{W} \frac{dW}{dp}$ at 0° C. unless otherwise stated.
55	Caesium .	20.3×10^{-6}	540×10^{-5} (0° to m.pt.)	Abnormal
56	Barium .	—	650×10^{-5}	Abnormal
57	Lanthanum .	57.6×10^{-6}	213 „	-1.20×10^{-6} (30° C.)
58	Cerium .	74 „	97 „	$+4.42 \times 10^{-6}$ (30° C.) (low pressure modification) -14.2×10^{-6} (30° C.) (high pressure modification)
	Rare Earth Group:			
72	Hafnium .	35.7 „	398 „	1.0×10^{-6} (30° C.)
73	Tantalum .	15 „	350 „	-1.49×10^{-6}
74	Tungsten .	5.48 „	510 „	-1.43 „
76	Osmium .	9.0 „	420 „	—
77	Iridium .	6.0 „	411 „	-1.35×10^{-6} (30° C.)
78	Platinum .	10.5 „	398 „	-1.98×10^{-6}
79	Gold .	2.4 „	400 „	-3.12 „
80	Mercury .	21.3 „ (- 50° C.)	—	—
81	Thallium .	18.1×10^{-6}	517×10^{-5}	-13.2×10^{-6}
82	Lead .	21.9 „	422 „	-14.4 „
83	Bismuth .	115 „	458 „	—
	Radioactive Elements:			
90	Thorium .	18 „	239 „	-2.79×10^{-6} (30° C.)
92	Uranium .	60 „	—	—

in 1876, several investigations have been made in order to test the validity of Ohm's Law, and at small current densities the Law is satisfied to the degree of accuracy with which the measurements can be made. But at current densities of the order 10^6 amperes per square centimetre, Bridgman¹ claimed in 1921 to have discovered a deviation from the Law of the order 1%. The method used in these experiments was to pass a large steady current through a very thin piece of metallic foil, and then to superimpose a small alternating current, when deviations from Ohm's

Law were shown by the differences between the resistances offered to the direct and alternating currents. In this way the temperature was the same for the two currents, and it was assumed that the small heating and cooling effect caused by the alternating current could be eliminated by working at several frequencies, and then extrapolating to infinite frequency. More recently the method has been examined in detail by Barlow,^{1a} who used a much wider range of frequencies, and showed that the extrapolation from the frequencies used by Bridgman was unjustified, and that no deviation from Ohm's Law could be detected for a gold film carrying a current of 2×10^6 amperes per square centimetre. For the present, therefore, no deviation from the Law has been satisfactorily established.

In order to obtain some idea of the magnitudes involved in connexion with the resistance and conductivity of pure metals, reference should be made to Tables I and II, in the third column of which the specific resistances of the elements are given, and it will be seen that these are of the order 10^{-5} to 10^{-6} ohms except for some of the borderline metals of Groups IV, V, and VI. No very obvious connexion appears to exist between the specific resistance of an element and its atomic weight or position in the Periodic Table of the Elements, and this is really only to be expected, since the specific resistance refers to unit volume, and there are of course different numbers of atoms in unit volumes of the different metals. In order to overcome this difficulty, Benedicks² suggested plotting the atomic number against the *atomic conductivity*, which is simply the specific conductivity divided by a factor proportional to the number of atoms in unit volume, and may be written C_{At} where $C_{At} = \frac{C}{d/A}$ where d is the density, and A the atomic weight. In this way it was shown that a distinctly periodic curve was formed, but the results were still complicated by the fact that the selection of any one arbitrary temperature was not the best way to bring out the underlying regularities. It was then shown by Benedicks, and later by Grüneisen,³ and Bridgman,⁴ that if all the specific conductivities were measured at a temperature equal to one-half the characteristic temperature of the metal,* a periodic curve was obtained

* The characteristic temperature on the Absolute scale is given by $\Theta = \beta\nu$, where ν is the characteristic frequency of the element, and $\beta = 4.78 \times 10^{-11}$ C.G.S. units. According to the Einstein theory of specific heats, Θ is the temperature at which the atomic heat equals 5.49. If for each metal we

of quite as definite a form as that given by the atomic volumes. Bridgman considered that the results were shown most clearly by plotting the atomic number against the conductivity per atom, which was defined as $\frac{C}{N^{\frac{1}{3}}}$, where N is the number of atoms per cubic centimetre, all conductivities being measured at half the characteristic temperature. The effect of the term $N^{\frac{1}{3}}$ is to give the conductivity between two atoms if a simple cubic packing be assumed, and strictly speaking a correction term is required for the effect of crystal structure. Since N is proportional to the reciprocal of the atomic volume, the conductivity per atom may also be written $C_{At}/(\text{Atomic Volume})^{2/3}$. The curve obtained in this way is shown in Fig. 1, and the following features are at once apparent:

(1) The conductivity per atom is much the greatest for the univalent metals of both long and short periods; i.e. for the alkali group and for copper, silver, and gold.

(2) There is always a sharp fall in the conductivity per atom in passing from a univalent element to the divalent element which follows it; e.g. from sodium to magnesium, or from silver to cadmium.

(3) On passing from the divalent to the trivalent elements of the same period, the effect is much less regular, and in some cases the conductivity per atom increases. As we shall show later in our general discussion, this fact, together with the relations for the inter-atomic distances, indicates that the atoms are not always fully ionized in the solid crystals of the Group III elements.

(4) The elements of Group IV A, carbon, silicon, titanium, and zirconium, have very small conductivities per atom, but in Group IV B, tin and lead have quite large conductivities, although germanium has not. As we shall see later (p. 326), the conclusion here is that in tin and lead the atoms are only partly ionized, whereas in the remaining elements the ionization is complete.

(5) In the transitional elements of the long periods, the conductivities per atom show a marked recovery at Group VI (chromium, molybdenum, and tungsten), after which there are irregular fluctuations until the sudden increase for copper, silver, and gold. Similar variations are also shown by the inter-atomic

make a temperature scale such that, starting from the Absolute zero, Θ is the unit temperature, the atomic heats of all metals are the same at equivalent points on these scales, and by comparing properties of different metals at equal fractions of the critical temperature, we tend to compare them under corresponding conditions as regards the atomic vibrations.

distances (see p. 320), and the conclusion is that, whilst in the *free atoms* of these elements the transition process begins at Group III (scandium, yttrium, and lanthanum), in the *solid crystal* the transition process begins at Group VI.

The above figures refer to metals in the normal polycrystalline condition, but methods have recently been developed for the production of large single crystals of metals, and the conductivities of these differ somewhat from those of the ordinary material. Thus the single crystals of copper prepared by Davey⁵ had a

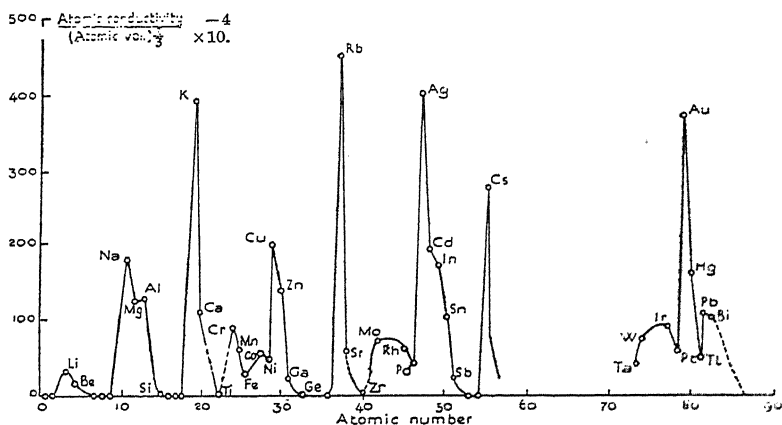


FIG. 1.

specific conductivity of 0.662×10^{-6} as compared with 0.584×10^{-6} for the same material in the polycrystalline state, and generally speaking single crystals have a slightly higher conductivity than the same metal in the normal condition.

In the case of cubic crystals it is always assumed that the symmetry conditions will make the specific conductivity and resistance independent of direction, but apart from some measurements on a naturally occurring crystal of copper referred to by Bridgman at the Solvay Congress in 1924, no conclusive proof of this appears to have been published. Recently it has been shown by M. Fraser* that with aluminium crystals the conductivity is independent of direction to within the limits of accuracy of the experimental methods ($\frac{1}{2}\%$), and this is in agreement with general theoretical conclusions.

For non-cubic crystals, however, it has been shown quite

* It is hoped to publish this work shortly.

conclusively that the specific conductivity is not independent of direction. The chief work in this connexion is due to Bridgman,⁶ and to Grüneisen and Goens,⁷ who have investigated the conductivities of single crystals of zinc and cadmium, whilst Bridgman has also examined bismuth, antimony, tellurium, and tin. Of these metals zinc and cadmium crystallize in the close-packed hexagonal structure; bismuth and antimony are also hexagonal, but the space group is 3 Di 5; tellurium is hexagonal with space group 3 D-4 or 3 D 6, whilst tin is tetragonal with space group 4 Di 19. In all these metals the resistance in any direction can be expressed in terms of two fundamental constants, namely W_{\parallel} , the resistance along the axis of three, four, or sixfold symmetry—according to the crystal structure—and W_{\perp} the resistance in any direction at right angles to such an axis.

TABLE III

Metal.	Axial Ratio.	Specific Resistance parallel and perpendicular to principal axes.	
		Grüneisen and Goens. for 0° C.	Bridgman. 20° C.
Zinc . . .	1.86	W_{\parallel} 5.83×10^{-6}	6.13×10^{-6}
		W_{\perp} 5.39 „	5.91 „
Cadmium . .	1.89	W_{\parallel} 7.79 „	8.30 „
		W_{\perp} 6.54 „	6.80 „
Bismuth . .		W_{\parallel}	138 „
		W_{\perp}	109 „
Antimony . .		W_{\parallel}	35.6 „
		W_{\perp}	42.6 „
Tellurium . .		W_{\parallel}	56,000 „
		W_{\perp}	154,000 „
Tin		W_{\parallel}	14.3 „
		W_{\perp}	9.9 „

The values for these constants as determined by Bridgman and by Grüneisen and Goens are shown in the above table. The resistance in any direction in these crystals is then given by the following expression which was first put forward by Voigt.⁸

$$= W_{\parallel} \sin^2 \alpha$$

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Here α is the angle between the particular direction considered and the axis of symmetry, whilst W_{\parallel} and W_{\perp} are the resistances parallel and perpendicular to the axis of symmetry.

With the hexagonal close-packed metals zinc and cadmium the ratios $\frac{W_{\parallel}}{W_{\perp}}$ are, at 0° C., 1.08 and 1.19 respectively, and are thus greater for the metal with the larger axial ratio. The variations of these ratios with temperature will be described later (see p. 16).

From the above description it can be seen that the specific resistance of a metal as ordinarily measured is not such a fundamental constant as might at first be imagined. For in the first place any measurement on polycrystalline metal involves the resistance of the intercrystalline material as well as that of the crystals themselves, whilst, apart from this, the resistance of a non-cubic crystal is itself a function of the direction relative to the crystal axes.

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2. The Effect of Temperature on Resistance

The specific resistance of a metal is also profoundly influenced by the temperature, the general rule being that rise of temperature increases the resistance, and, at ordinary and higher temperatures, the specific resistance is, to a first approximation, directly proportional to the absolute temperature for the majority of metals. The so-called 'temperature coefficient' is usually measured between 0° and 100° C., and may be denoted by α where

$$\alpha = \frac{1}{W_0} \cdot \frac{W_{100} - W_0}{100}$$

where W_0 and W_{100} are the specific resistances at 0° and 100° C. respectively. If the specific resistance were exactly proportional to the absolute temperature, the value of α would be $\frac{1}{273}$ or about

0.0037, but the actual values for pure metals are in nearly all cases greater than this, as can be seen from Table I.

To a higher degree of accuracy, the relation between temperature and specific resistance is not exactly linear, the resistance usually increasing more rapidly as the temperature rises, although exceptions are shown by some metals such as platinum, palladium, and tantalum. At present no very general law covering these variations has been discovered, although the slight curvature of the temperature-resistance curves can be allowed for by empirical equations of the usual parabolic type, such as $W = a + b\theta + c\theta^2$, where c is positive for most metals, but negative for others such as platinum.

Since the relations between temperature and resistance are not strictly linear, we have for precise comparison to deal with the 'instantaneous temperature coefficient' at a given temperature, and this is given by $\frac{1}{W} \frac{dW}{d\theta}$, and may be determined either by drawing tangents to the temperature-resistance curves, or by assuming some empirical equation such as $W = a + b\theta + c\theta^2$, and then finding the values of a , b , and c which agree best with the observations, when the values of $\frac{dW}{d\theta}$ can be obtained.

The alkali metals, and the magnetic metals of the first long period (iron, cobalt, and nickel), are remarkable for the high values of their temperature coefficients, whilst the curvature of the temperature-resistance curves is much more pronounced in the case of the last three metals. In the case of the alkali metals an abnormal increase in the resistance takes place just below the melting-point, although the melting process itself takes place quite sharply at constant temperature. This increase in resistance is accompanied by an increase in thermo-electric power (see p. 100), and by a fading out of the X-ray diffraction patterns, and it appears to indicate that some kind of a loosening of the lattice occurs before the actual melting.

It is, however, at very low temperatures that the metallic elements show their most interesting characteristics, and under these conditions they divide themselves into two main classes, namely, those elements which show supra-conductivity, and those which do not. As far as the direct experimental evidence goes at present, the second class is the more general one, and we may therefore deal with this first, taking as a typical example the case of the metal gold. For this metal down to about 100° Abs. the rela-

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tion between temperature and resistance is approximately linear, and may be expressed by a relation of the type $\frac{W_\theta}{W_{273}} = \alpha(\theta - \phi)$ where α and ϕ are characteristic constants. At very low temperatures, however, the curve begins to flatten and eventually becomes parallel to the temperature axis, that is to say, the resistance reaches a constant value which is independent of temperature. The actual values obtained by Onnes¹ for two

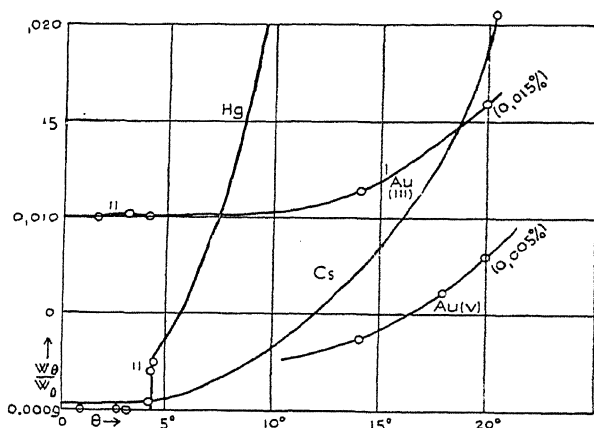


FIG. 2. Showing resistance of gold, caesium, and mercury at low temperatures. The curves show $\frac{W_\theta}{W_0}$ plotted against θ , where W_0 is the resistance at 0° C. The figures on the curves for gold give the percentage of impurity.

different samples of gold are shown graphically in Fig. 2, and it will be seen that the limiting constant value which the resistance attains at very low temperatures is different in the two cases. The resistance of a metal under these conditions is in fact very sensitive to the exact state of the specimen as regards impurities, internal strains, &c., but it has been shown by Onnes and his collaborators that if the resistance-temperature curves for a number of specimens of the same metal be plotted graphically, the different curves can be almost exactly superposed if each is moved a certain distance parallel to the resistance axis. This is taken to indicate that the actual resistance is composed of two parts, an 'ideal resistance' characteristic of the pure metal, and an additional resistance caused by the presence of impurities, strains, &c. In any one specimen, the additional resistance is

independent of temperature over a considerable range, but it varies with the degree of strain, and the amount and nature of the impurity. As the metal becomes purer, the curves pass nearer to the origin, and the 'ideal resistance curve' is determined by using very pure specimens, and then displacing the measured temperature-resistance curve so that it passes through the origin (i.e. so that $W = 0$ at 0° Abs.). At high temperatures the ideal resistance varies linearly with the temperature, but the curves flatten as the absolute zero is approached, and we shall deal later (p. 17) with the equations suggested to cover these curves.*

The second class of metals show supra-conductivity, and are of very great interest, and in order to describe their behaviour we may deal with the case of mercury for which the temperature-resistance relations are shown in Fig. 2, which is taken from the well-known work of Onnes and his collaborators.² In this case it will be seen that down to about 5° Abs. the resistance varies with the temperature in the normal way, but that at still lower temperatures a point is reached at which the resistance suddenly drops to an almost imperceptible quantity. It has in

TABLE IV

<i>Metal.</i>	<i>Temperature at which supra-conductivity appears.</i>
	K.
Lead . . .	7.2°
Tantalum . . .	4.5°
Mercury . . .	4.16°
Tin . . .	3.72°
Indium . . .	3.40°
Thallium . . .	2.47°
Thorium . . .	1.4°
Gallium . . .	1.07°

* For many purposes in low temperature work it is more convenient to deal with the ratio of the resistance (W_θ) of the specimen at a particular temperature to that of the same specimen at 0° C. (W_0), since in this case $\frac{W_\theta}{W_0}$ is independent of the size of the specimen. In this case if we put $\frac{W_\theta}{W_0} = \omega$, the curves for specimens of the same metal differing as regards impurities, strains, &c., are such that $\omega_1 - \omega_2 = \lambda (1 - \omega_2)$ where ω_1 and ω_2 refer to the two specimens and λ is independent of temperature. This was shown by Nernst (*Sitz. Ber. Berlin Akad.* 1911, 314; also Onnes and Bergers, *Proc. Akad. Amsterdam*, 1918, 20, 1163). This may readily be deduced from the fact that the W curves can be superposed. See p. 10 above.

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fact been shown by Onnes that, in the case of lead, the resistance below this critical temperature is less than 10^{-12} of its value at 0°C . Under these conditions if a current is once started in a closed ring by a magnetic field, it will continue for many hours without any perceptible decrease in strength, and will in fact require several months for its strength to diminish by one-half. A metal in this state is said to exhibit *supra-conductivity*, and each metal which shows this phenomenon enters the supra-

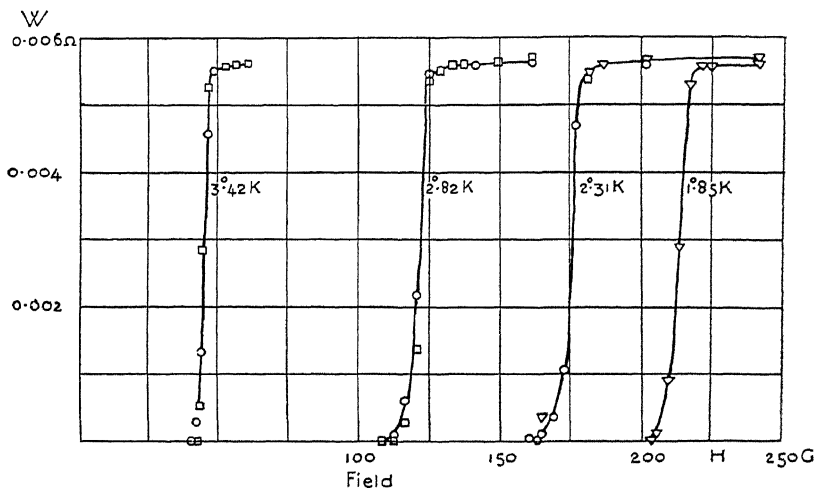


FIG. 3. Showing the change in resistance (W) of tin caused by the application of an external magnetic field of strength H .

conducting state at a definite temperature. These characteristic temperatures for the eight metals for which the phenomenon has been observed are given in the table on page 11. In the case of tantalum, according to Meissner,¹⁰ the change is not quite so sharp.

Supra-conductivity below these temperatures can, however, be destroyed by the application of an external magnetic field of sufficient strength, and the minimum field strength required in order to give the metal a finite resistance is known as the threshold value, which is increased as the temperature is lowered. The way in which the resistance varies as the magnetic field is increased is shown in Fig. 3 for the case of tin, and it will at once be seen that the change is comparatively sharp. The relation between the temperature and magnetic threshold is, to a first approximation, of the type

where H_0 represents the (hypothetical) value of the magnetic threshold at the absolute zero, and $C_{H\theta}$ is a constant which is very nearly the same for all the supra-conducting metals. These results are shown graphically in Fig. 4, the numerical data being given in Table V, which is taken from the work of Sizoo,³ and of Onnes and Tuyn.⁴ From this it will be seen that the slopes of the lines for the different metals are all very nearly the same, and that, to a higher degree of accuracy, the points do not lie on straight lines, but on curves which are slightly concave towards the origin.

With normal polycrystalline metals these values show an hysteresis effect, and are not the same when the point is approached with increasing and diminishing fields. Investigations

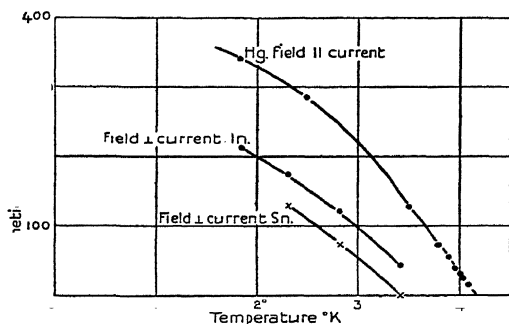


FIG. 4.

by de Haas and Onnes,⁵ and de Haas and Voogd,^{5a} have shown that this is a definite characteristic of all supra-conductors, and that it is shown in its purest form by single crystals, for which the curves connecting resistance and field strength show a series of definite jumps or discontinuities, which become smoothed out in polycrystalline metal.

It was shown by Onnes⁶ that the supra-conductivity phenomenon is also destroyed when the strength of the current in the metal exceeds a certain critical value, but when the current strength is measured per unit cross-section of the wire used, the critical values vary with the diameter of the wire, and it was first suggested by Silsbee⁷ that the value of the critical current was that at which the magnetic field due to the current itself became equal to the magnetic threshold value, which, as we have already seen, is the value of the magnetic field necessary to destroy the supra-conductivity. If this were so the values

TABLE V

<i>Metal.</i>	<i>Temperature (θ).</i>	<i>Mean Value of Magnetic Threshold.</i>	
		<i>Magnetic Field \perp current.</i>	<i>Magnetic Field \parallel current.</i>
Mercury .	4.097° Abs.	—	13.1 Gauss
	4.036 "	—	23.7 "
	4.002 "	—	30.0 "
	3.963 "	—	38.4 "
	3.883 "	—	54.7 "
	3.797 "	—	70.2 "
	3.498 "	—	127 "
	2.493 "	—	286 "
	1.813 "	—	340 "
Indium .	3.41 "	0 Gauss	—
	2.82 "	74 "	—
	2.31 "	130 "	—
Tin A .	3.42 "	44 "	—
	2.82 "	121 "	—
	2.31 "	174 "	—
	1.85 "	212 "	—
Lead A .	7.2 "	0 "	—
	4.3 "	520 "	—
	4.18 "	537 "	—
	3.73 "	601 "	—

TABLE VI

<i>Metal.</i>	<i>Temp.</i>	<i>Cross-section of Specimen in sq. mm.</i>	<i>Critical Current Density in Amp./mm.²</i>	<i>Induced Magnetic Field $\frac{2C_c}{r}$.</i>
Mercury	4.1°	0.0016	107	15
	—	0.0025	69	12
	—	0.0055	42	11
	—	0.0055	58	15
	3.6°	0.0016	625	89
	—	0.0025	427	76
Thallium	2.47°	0.2	0.6	1
	2.45°	0.2	1.3	2
	2.43°	0.2	3.2	5
	1.38°	0.2	18	29
	1.36°	0.031	50	31
Lead	4.21	0.059	407	356
	4.21	0.025	680	385

obtained for the critical current density at any one temperature should vary with the radius of the wire in such a way that $\frac{2C_c}{r}$ remained constant, since this expression gives the strength of the induced magnetic field (C_c is the critical current density and r the radius of the wire). As Table VI on p. 14 shows, this condition is approximately fulfilled, and the calculated values of the induced magnetic field are in very fair agreement with those for the magnetic threshold given in the preceding tables.

It has recently been found by Onnes and Sizoo⁸ that the critical temperature at which supra-conductivity occurs is *raised* when the wire is subjected to a tension within the limits of elasticity, a result which was quite unexpected. Thus with a wire of tin, a tension of 2.5 Kg. per sq. mm. raised the critical temperature by about 0.02°. On the other hand the critical temperature is lowered by hydrostatic pressure.

These very remarkable phenomena have naturally aroused much interest, and particular attention has been given to the question whether a sudden change takes place in any of the other properties of metals when they enter the supra-conducting region, but up to the present the evidence on this point is entirely negative. It has been shown by Onnes and Keesom⁹ that no change in crystal structure takes place when lead becomes supra-conducting, whilst the thermal conductivity is also unaffected. These observations show that the phenomenon of supra-conductivity cannot be due to a simple polymorphic transformation as had sometimes been imagined.

Considerable attention has been paid to the question whether supra-conductivity is a characteristic of some metals only, or a general property of all the metallic elements. At present the evidence on this point is very confusing, but considered purely from the experimental point of view the results appear to indicate that some metals are not supra-conductors. In particular it has been shown by Meissner,¹⁰ Onnes and Tuyn,¹¹ McLennan and his collaborators,¹² and by de Haas, Sizoo, and Voogd,^{13, 14} that the following metals retain a finite resistance at the lowest temperatures attainable by means of liquid helium; lithium, sodium, potassium, rubidium, caesium, copper, silver, gold, beryllium, zinc, cadmium, aluminium, iron, cobalt, nickel, platinum, germanium, hafnium, and zirconium, all in the polycrystalline condition, and single crystals of arsenic and antimony.

Criticism of these results has been made on the grounds that

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impurities might be present in some cases and not in others, so that the whole subject is at present rather obscure, and the theoretical conclusions will be described later (p. 337).

The metals for which supra-conductivity has at present been observed are: mercury, lead, thallium, indium, tin, tantalum, gallium, and thorium. In the case of tin it is the tetragonal form (white tin) which exhibits supra-conductivity, and not the cubic (diamond structure) grey tin.

The Resistance of Single Crystals at Low Temperature.

In the preceding section we have seen that for the crystals of non-cubic metals investigated by Bridgman and by Grüneisen and Goens, the resistance can be expressed in terms of the resistances

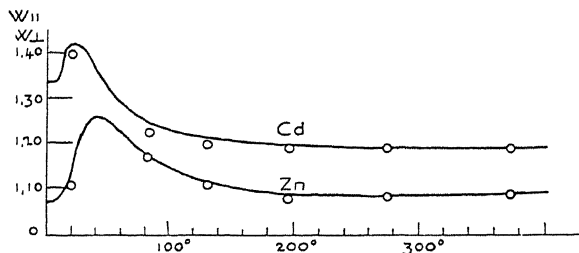


FIG. 5. The effect of temperature upon the ratio of the specific resistance parallel (W_{\parallel}) and perpendicular (W_{\perp}) to the hexagonal axis of single crystals of zinc and cadmium.

and W_{\perp}) parallel and perpendicular to the principal axis. Both W_{\parallel} and W_{\perp} diminish with falling temperature, and the ratio $\frac{W_{\parallel}}{W_{\perp}}$ does not remain constant, but, as shown in Fig. 5, rises to a maximum in the neighbourhood of about 40° Abs. (—230° C.), which is in the region where the atomic heats begin to diminish abnormally (see also p. 115).*

The Equations of Gruneisen.

We may now refer to some relations discovered by Grüneisen which are of interest both theoretically and as empirical relations between the resistance and temperature. In 1913 Grüneisen¹⁵ discovered that at low temperatures the specific resistance W of a pure metal was approximately proportional to the product

* It should be noted that the above figure represents the ratio $\frac{W_{\parallel}}{W_{\perp}}$ estimated for perfectly pure metal, the slight additional resistance caused by impurities having been deducted.

of the absolute temperature and the atomic heat (C_p), so that one could write

$$W \propto \theta C_p \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Grüneisen then showed further¹⁶ that in many cases over a wide range of temperature, the above first approximation became more accurate if expressed in the form

$$W \propto \theta \cdot F\left(\frac{\theta}{T}\right) \frac{C_p}{T} \quad (2)$$

Here F is the function of Debye for the atomic heat C_v ,¹⁷ but in place of the characteristic temperature Θ_0 of the specific heat theory, use is made of a new characteristic temperature Θ_r , which has to be determined from the resistance measurements, and which is slightly different from Θ_0 . At low temperatures this type of relation gave a good agreement between the observed and calculated values in many cases, as may be seen from the following table, which gives the results for platinum.

TABLE VII

Temperature. °Abs.	Observed Value of W .	Estimated Value of W for Pure Platinum (Ideal Resistance).	Calculated Value of W .
14.2	0.0107	0.0007	0.00096
17.9	0.0124	0.0024	0.00245
20.3	0.0142	0.0042	0.00402
56.5	0.1102	0.1013	0.1036
68.4	0.1597	0.1512	0.1537
90.3	0.2528	0.2453	0.2484

This relation, however, breaks down completely at very low temperatures, and for some metals it also fails at high temperatures. It is concluded that the function F is not really exactly the same as the Debye atomic heat expression, and that this difference is to some extent allowed for by the combined effect of the $\frac{C_p}{C_v}$ term and the substitution of Θ_r for Θ_0 , but that this is not sufficient in all cases. At higher temperatures, however, it is well known that the resistance can be expressed accurately by empirical equations of the type $W = 1 + a\theta + b\theta^2$, and in a later paper¹⁸ Grüneisen has succeeded in combining an empirical equation of this type with the older expression for the results at low temperatures, and in this way a single equation is obtained which

covers the facts satisfactorily over a very wide range. This equation is of the form

Here F is again the Debye atomic heat function, Θ_r is the appropriate characteristic temperature which has to be determined from the resistance measurements, and a and b are further constants, so that the equation involves three constants which have to be determined by measuring the resistance at three different temperatures. At high temperatures, however, the $F\left(\frac{\theta}{\Theta_r}\right)$ term becomes constant, so that the expression is of the well-known empirical type with two constants only. It must be understood, however, that these equations refer to very pure metals, free from strain or other physical abnormality. In the case of metals with a large additional resistance, the equation is useless at low temperatures unless the resistance is corrected (by the subtraction of a constant amount) to allow for the effect of impurities, strains, &c. The values of the constants a and b differ considerably from one metal to another; a is positive and is of the order 10^{-3} to 10^{-4} ; whilst b is smaller, and may be either positive as in the case of gold, or negative as with platinum.

Abnormal Metals.

The relations described above refer to what may be called normal metals, but apart from these there are a few elements, usually classed as metals, which behave quite abnormally. These are confined to Groups IV, V, and VI of the Periodic Table, and are never found in the earlier groups. In Group IV, germanium and titanium have negative temperature coefficients of resistance at low temperatures. On raising the temperature, the resistances pass through minima, and then increase, after which the effects become complex. The temperatures of the minimum resistances are $+100^\circ\text{C}$. for titanium, and -116°C . for germanium, and are thus higher for the element of lower atomic weight. With silicon, of still smaller atomic weight, the temperature coefficient is negative up to high temperatures at which polymorphic transformations occur, and obscure the minimum which presumably would otherwise be shown. In the case of germanium it has been shown by Bidwell¹⁹ that the data are covered satisfactorily by an equation of the type

$$\frac{1}{W} \cdot \frac{dW}{d\theta} = -\left(\frac{Q}{k}\right) \frac{1}{\theta^2} + a$$

which is the derivative of $W = Ae^{\left(\frac{Q}{k\theta} + a\theta\right)}$. As we shall show later (p. 309), the conclusion to be drawn from this is that these elements are not really true metals at all in the pure crystalline state at low temperatures, but co-valent (homopolar) substances in which electrons are set free by raising the temperature or by impurities.

Abnormal results are also shown by the elements in the fifth and sixth B sub-groups. Arsenic, antimony, and bismuth are characterized by retaining an abnormally large resistance at the lowest temperatures attainable with liquid helium, although the resistances diminish continually as the temperature is lowered. On the other hand, in the case of tellurium, although the temperature coefficient is fairly normal at 0° C., the phenomenon of a minimum resistance is again found although at a very low temperature (—225° C.). Selenium shows the well-known effect in which the resistance varies under the influence of light, and in both these Group VI metals the conductivity varies considerably with the applied potential, so that Ohm's Law breaks down. The resistance of selenium diminishes on illumination, but the effect is complex and we shall not consider it further, because these so-called metals are essentially abnormal, and do little to throw light on the general principles underlying metallic conduction.

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3. The Effect of Pressure on Resistance

Effect of Pressure.

The resistance of a metal is also affected by the external pressure, the general effect being that an increase in pressure lowers the resistance. In this connexion it is necessary to distinguish between two effects, the change in specific resistance of a metal under pressure, and the change in resistance of any given sample. For when a metal is compressed, its volume is altered, and hence the change in resistance of a piece of wire under pressure needs correction before it gives the change in specific resistance. We are here, of course, dealing with volume compression in which the pressure is exerted equally on all sides, and not with longitudinal compression exerted in one direction only.

Really accurate work over a wide range of pressure has recently been carried out by Bridgman,¹ who has determined the resistances of many metals at pressures up to 12,000 Kg./cm.², and at different temperatures. As this work is much more complete and accurate than any of the preceding determinations, we may consider it alone, although earlier work has been carried out by Beckman and others, to whose work references will be found in Bridgman's papers.

Bridgman classifies metals in either the liquid or solid states as normal if their resistance be diminished by pressure, and abnormal if the resistance be increased, and in this way the lists on the opposite page are obtained.

Of the abnormal metals, caesium, rubidium, and barium are unique in that with increasing pressure the specific resistance passes through a minimum, and then begins to increase. The metals which show this phenomenon possess high atomic

Normal Solids.

Copper	Thallium	Cobalt
Silver	Silicon	Nickel
Gold	Titanium	Palladium
Beryllium	Zirconium	Platinum
Magnesium	Tin	Lanthanum
Zinc	Lead	Neodymium
Cadmium	Arsenic	Praseodymium
Mercury	Tantalum	Thorium
Aluminium	Molybdenum	Zirconium
Gallium	Tungsten	Hafnium
Indium	Iron	

Abnormal Solids.

Normal Liquids.

<i>Minimum Resistance at</i>					
Barium	.	.	.	8,600 Kg./cm. ²	Sodium
Caesium	.	.	.	4,200 " "	Potassium
Rubidium	.	.	.	17,800 " "	Bismuth

*Probable Minimum Resistance
(obtained by extrapolation) at*

Potassium	.	.	.	23,500 Kg./cm. ²	
Sodium	.	.	.	28,000 " "	
Lithium	.	.	.	Positive Pressure Coefficient	
Calcium	.	.	.	" " "	
Strontium	.	.	.	" " "	
Titanium	.	.	.	" " "	
Cerium	.	.	.	" " "	
Antimony	.	.	.	" " "	
Bismuth	.	.	.	" " "	

Abnormal Liquids

Lithium

volumes and high compressibilities, and by an analysis of the resistance-pressure curves for sodium and potassium, Bridgman² has concluded that these would also show minimum resistances at about 28,000, and 23,500 Kg./cm.² respectively, these pressures being higher than those which can be obtained experimentally. It is for this reason that we classify sodium and potassium as abnormal metals. Since lithium shows a positive pressure coefficient at all pressures, the conclusion is that at sufficiently high pressures all the alkali metals have positive pressure coefficients of resistance. Lithium, however, is quite out of sequence, since in passing from caesium to sodium the pressure corresponding to the minimum resistance increases, and we should therefore expect lithium to show a negative coefficient up to a very high pressure, whereas actually its coefficient is positive throughout. But for other metals, apart from barium, any possible minimum would lie far above the pressures which can now be reached experimentally.

22 *The Electrical Conductivity of Pure Metals*

The abnormal metals are confined chiefly to the alkali and alkaline earth sub-groups, and to the border-line metals antimony and bismuth, but since the abnormality is not always of the same type it can hardly be said that there is any definite correspondence between the position of the metal in the Periodic Table, and the effect of pressure.

Some idea of the magnitude of these effects should be gained, and for this purpose we may consider first the normal metals in which the resistance diminishes under pressure. The results may be expressed in two different ways, either in terms of the rate of change of resistance compared with that of pressure, or in other words in terms of $\frac{dW}{dp}$, which is negative for the normal metals, or else in terms of the 'instantaneous pressure coefficient' which is given by the expression $\frac{1}{W} \frac{dW}{dp}$. For many purposes the latter is usually preferred since it gives the fractional change in resistance at any point, but in some ways its use is rather unfortunate as it tends to obscure a simple linear relation. Thus, if the relation between pressure and resistance be linear, the value of $\frac{dW}{dp}$ is constant, but the instantaneous pressure coefficient becomes numerically greater with pressure, since W becomes smaller and the term $\frac{1}{W}$ larger.

To a first approximation, the relation between pressure and resistance can be considered as linear, the initial value of the instantaneous pressure coefficient at zero pressure being of the order 10^{-5} to 10^{-6} for most metals. To a greater degree of accuracy the relation is not strictly linear, but the initial rate of decrease is greater than at higher pressures. This departure from linearity is generally greater for those metals which have (numerically) greater pressure coefficients, and it varies from about 0.8% to 5% of the total change in resistance under 12,000 Kg./cm.² pressure. The departure from linearity also depends upon the temperature, but it does not seem possible to express any of these deviations by equations which are common to all metals.

The pressure coefficients at ordinary temperatures are only very slightly affected by temperature, and, conversely, the temperature coefficient of resistance is almost unaltered by pressures up to 12,000 Kg./cm.² This is in some ways very remarkable,

for at these high pressures the centres of the atoms are closer together than they would be at the absolute zero of temperature under normal pressure, but in spite of this the relative increase in resistance produced by a rise of 1°C . is practically the same at 12,000 Kg./cm.² as at normal pressure. This indicates very clearly that the mean distance between the atoms, as measured by the external dimensions of the solid, is not the important factor in determining the resistance.

To a greater degree of accuracy, the pressure coefficients of the normal metals are slightly increased by a rise of temperature, but this effect is very small. An exception is presented by tungsten, for which the pressure coefficient is less at 50°C . than at either 0° or 100°C . All these results refer to measurements at normal or moderate temperatures, and the effect of pressure at very low temperatures has not yet been examined.

In order to give a general idea of the magnitude of these effects, the instantaneous pressure coefficients at zero pressure are given in column 5 of Table I (p. 2). It will be noted that the alkali metals have the highest coefficients.

As for the other abnormal solids, antimony, bismuth, calcium, strontium, and lithium, little useful generalization can be made, except that the instantaneous pressure coefficients increase slightly with rising pressure, and diminish very slightly with rising temperature, although strontium is an exception as regards the pressure effect.

We may summarize these most interesting results by saying that the effect of pressure on resistance is comparatively slight, and that, in the great majority of cases, it diminishes the resistance. On the other hand the exact details of the pressure variation, and the abnormal behaviour of some metals appear to permit of no generalization, and the fundamentals are not yet understood.

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4. Effect of Stress and Deformation upon Resistance

In the work on the effects of pressure upon the resistance of pure metals which we have described above, we have been dealing with metals under a volume compression exerted equally on all sides. Under these conditions the metals are perfectly elastic, and return to their normal condition when the pressure is withdrawn. On the other hand, in the case of simple tensile or compressive stresses, the range of elasticity is very small, and is readily exceeded by the forces which are at our disposal. When this happens the great majority of metals and solid solutions undergo plastic deformation which is permanent, and remains after the stress is withdrawn. Metals in this condition are said to be 'worked', and terms such as 'cold-worked', 'hot-rolled', &c., are used to describe the conditions under which the deformation is carried out. In considering the effect of deformation upon resistance we have, therefore, to distinguish carefully between deformation within the elastic limit, and deformation resulting in a permanent change in size. With the softer metals, such as copper, the elastic range is so small that it is almost impossible to make measurements within the elastic limit. This difficulty is particularly marked when we come to deal with single crystals of these metals, since in many cases these crystals are so soft that mere handling results in a permanent deformation. We may consider first the effect upon resistance of a tensile stress within the elastic limit.

Effect of Tension within the Elastic Limit.

In considering the effect of tension we have to take into account the change in resistance in the direction of the tensile stress, and at right angles to it. Of these two, the longitudinal change in resistance is by far the more easy to measure, and determinations of this kind were made by Tomlinson¹ as long ago as 1883. These determinations have recently been repeated by Bridgman,² and as this investigator used purer materials and more refined methods, we may consider his results alone, especially as the majority of the earlier workers did not appreciate the distinction between elastic and permanent distortion.

In the great majority of cases, the effect of a tensile stress within the elastic limit is to increase the longitudinal resistance of the metal, that is, the resistance in the direction of the tensile stress. These effects are comparatively slight, and when the stress is expressed in Kg./cm.² the instantaneous tension coefficient of resistance $\left(\frac{1}{W} \frac{\partial W}{\partial T}\right)$ is of the order 10^{-6} , as can be seen from the following table.

It is naturally a matter of interest to see whether the metals which behave abnormally under hydrostatic pressure are also abnormal under tension, but it seems that no definite connexion exists between the two phenomena. Thus bismuth and strontium are abnormal both under pressure and tension, but lithium, calcium, and antimony, although abnormal as regards the pressure effect, are quite normal in tension. These results are collected in Table VIII in order that a general idea may be obtained of the magnitudes involved.

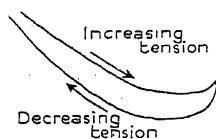
TABLE VIII

<i>Metal.</i>	<i>Tension Coefficient of Specific Resistance.</i>			
Aluminium . . .	+	1.8	$\times 10^{-6}$	at 20° C.
Copper . . .	+	1.6	"	" "
Silver . . .	+	3.1	"	" "
Iron . . .	+	1.8	"	" "
Palladium . . .	+	1.6	"	" "
Platinum . . .	+	1.6	"	" "
Lithium . . .	+	11	"	" 30° C.
Calcium . . .	+	0.8	"	at room temperature
Strontium . . .	-	21.2	"	" "
Antimony . . .	+	3.0	"	" "
Bismuth . . .	-	3.65	"	" "
Cobalt . . .	+	0.19	"	" "

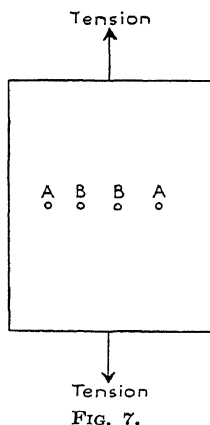
The high value for lithium is possibly due to the elastic limit having been exceeded, since this metal is so soft that great difficulty was experienced in the manipulation.

The metal nickel presents a very curious exception to the general rule. It is an abnormal metal in the sense that its resistance decreases under tension, but in contrast to the other metals this decrease is not approximately proportional to the tension. The resistance in fact passes through a minimum and begins to increase again after a certain tension is exceeded. In this case, if the elastic limit be not exceeded, measurements made with increasing and diminishing tension show open hysteresis loops.

These, however, differ from the usual hysteresis loops in that at the initial stages of the decreasing limb of the loop the resistance may be lower than that corresponding to any value of the tension on the increasing loop. Typical results of this nature are shown in Fig. 6 and are probably connected with the low temperature polymorphic transformation of nickel.



Tension
FIG. 6.



Tension
FIG. 7.

Whilst the longitudinal effect of tension on resistance is fairly easy to measure, the transverse coefficient is very much more difficult. With specimens in the form of wires or thin rods such as are generally used for conductivity measurements, it is practically impossible to obtain a simple tensile stress at right angles to the axis. On the other hand, if one uses a large sheet which can be stretched in tension, the simple transverse resistance can only be obtained if the conditions of flow of the current be known, and difficulties arise in connexion with irregularities in the neighbourhood of clamps, fasteners, &c.

The method adopted by Bridgman³ was to stretch a sheet of metal as shown diagrammatically in Fig. 7, and then to lead a current through the metal from the contacts A A, and to measure the potential difference between the intermediate points B B. These measurements do not give the actual transverse resistance, but by a somewhat detailed

mathematical argument it can be shown that they are connected with the ratio of the longitudinal and transverse resistances, so that this ratio can be found, and then a second determination of the longitudinal coefficient alone enables the transverse coefficient to be calculated. Table IX shows the results obtained in this connexion.

The slight differences between the values given here for the longitudinal coefficients, and those in the previous table, are due to the use of different specimens, since the sheets of metal used were not always of the same purity as in the other work.

From these figures it can be seen that the transverse effect is usually smaller than the longitudinal, and that the signs of the two coefficients may or may not be the same.

In the case of nickel the results are again very confusing. The signs of the two coefficients are different, but the actual values show marked hysteresis effects, and depend also on the previous treatment of the sheet as regards rolling, annealing, &c.

TABLE IX

<i>Metal.</i>	<i>Longitudinal Coefficient of Specific Resistance. Tension in Kg./cm.²</i>	<i>Transverse Coefficient of Specific Resistance. Tension in Kg./cm.²</i>
Gold . .	+ 3.87 × 10 ⁻⁶	- 4.9 × 10 ⁻⁶
Silver . .	+ 2.86 „	- 0.04 „
Copper . .	+ 1.75 „	- 2.4 „
Palladium . .	+ 1.37 „	+ 0.51 „
Platinum . .	+ 1.78 „	+ 0.34 „
Iron . .	+ 1.42 „	+ 0.54 „

Effect of Permanent Deformation upon Resistance.

Up to the present we have only been referring to the effect of stresses within the elastic limit of the metal, but when this limit is exceeded and permanent distortion occurs, the changes become more complex. If the metal is deformed by rolling, stretching, &c., and the force producing the distortion is then removed, a permanent increase in resistance is observed, and may amount to as much as 8 to 10% of the total resistance. Thus Beilby⁴ in his book on the *Aggregation and Flow of Solids* gives the increase in resistance as 8, 2.5, and 1.8% respectively for silver, copper, and gold, whilst for aluminium of 99.9% purity work by Holborn⁵ gave the specific resistances in the normal and worked states as 2.53×10^{-6} and 2.61×10^{-6} respectively. The exact values depend on the amount and nature of the deformation, and as these are, of course, purely arbitrary, no very definite standard of comparison can be obtained. These figures refer to the normal material after the withdrawal of the stress, but if a tension be again applied within the limits of elasticity of the deformed metal the resistance is once more affected by tension as in the case of unstrained metals, although these effects have not been studied in detail.

The methods of X-ray crystal analysis have shown that deformation such as occurs in the rolling of a polycrystalline metal

results in the elongation of the crystal grains, so that they gradually take up a preferred orientation, the relation of which to the crystal axes can be calculated if the nature of the deformation of a single crystal be known. The increase in resistance of a metal after permanent deformation is, however, much greater than can be accounted for by changes in orientation, and is mainly due to a strained condition existing inside or between the crystal grains, or along the planes on which slipping has occurred in the individual crystals. The exact nature of what is commonly called 'strained metal' is, however, little understood. In the case of copper it has been shown by Tammann and Straumaris⁶ that if annealed copper wire be reduced about 30% by drawing, practically all the crystals have rhombic dodecahedral planes in the longitudinal section of the wire, and the usual slight increase in resistance occurs. If now the wire be annealed at 250° C., only 2% of the deformed crystals change their orientation, whilst no less than 70% of the increase in resistance which occurred on deformation is found to vanish, showing that the straining of the metal, and not the preferred orientation, is the cause of the change in resistance.

As is only to be expected, the permanent deformation of metals produces slight changes in many of the electrical properties associated with the conductivity. Thus the temperature coefficient of resistance of a metal is generally lowered by working, the values given by Holborn for aluminium in the 'hard' (i.e. worked) and soft states being 0.00429 and 0.00443 respectively. In cases of this kind where temperature variations are involved it is necessary to distinguish between changes in the temperature zone where results are reproducible, and those in which the temperature becomes sufficiently high to relieve the strain or to allow the metal to recrystallize.

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5. Galvano-Magnetic and Thermo-Magnetic Effects

A. The Effect of a Transverse Magnetic Field.

The resistance of a metal is also affected by the presence of a magnetic field, although the magnitude of this change is comparatively slight in all except a few metals. The action of a transverse magnetic field causes a number of small changes, and these may conveniently be grouped together although they do not refer exclusively to the electrical conductivity. These effects may be most simply explained by imagining that an electric current flows down a rectangular metal plate, and that a magnetic field is applied at right angles to the direction of the current, and at right angles to the plate. Under these conditions a number

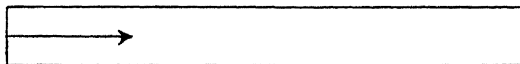


FIG. 8.

of phenomena are observed and may be described under the following headings.

1. *The Transverse Effect* (Longitudinal Hall Effect). When a magnetic field is applied at right angles to the current, an increase in the longitudinal resistance of the specimen is produced, and is sometimes called the Longitudinal Hall Effect, but more generally the *Transverse Effect*, which is particularly marked in the case of bismuth. For the more normal metals the effect is much less pronounced, being less than 0.01% for a field of 10,000 C.G.S. units, and it is only since the recent development of methods for producing very strong magnetic fields that the process has been examined in detail by Kapitza,¹ who has investigated the behaviour of a large number of metals at fields up to 300 kilogauss.

The ferro-magnetic metals iron, nickel, and cobalt behave abnormally, but, apart from these, the normal metals all show the same general behaviour when placed in a transverse magnetic field, the change of resistance being proportional to the square of the field strength in weak fields, and directly proportional to the field strength in strong fields. The general type of the curves connecting field strength and change of resistance is thus as shown in Fig. 9, the upper portion of the curve being a straight line, whilst the lowest portion follows a square law,

and the experimental results can be expressed within the limits of accuracy of the measurements, by the two equations

$$\text{Weak Fields: } \frac{\Delta W}{W} = \beta \frac{H^2}{3H_k}$$

$$\text{Strong Fields: } \frac{\Delta W}{W} = \beta \left(H - H_k + \frac{H_k^2}{3H} \right)$$

where H_k is the intercept made by the asymptote to the linear portion of the curve on the axis representing field strength. The

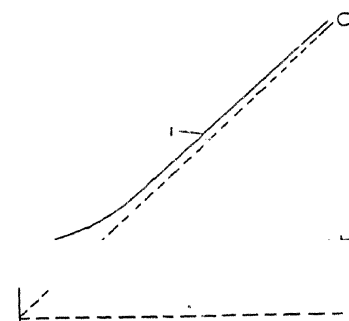


FIG. 9.

change from the square to the linear law takes place gradually after a critical field strength which may vary from 5 to 250 kilogauss according to the metal.

It was then shown by Kapitza that the upper linear portions of the curves were independent of the exact physical state of the metal as regards strains, &c., and were also probably unaffected by very small amounts of impurity,* but that the lower parts of the curves were very much affected by the

exact condition and purity of the metal. These results have been taken to indicate that the actual resistance of the metal is composed of two parts, an ideal resistance which obeys the linear law, and an additional resistance caused by impurities, internal stresses, and similar factors. From this point of view the important constant is the factor β in the above equations, and this increases very greatly as the temperature is lowered, as can be seen from Table X which gives some of the results obtained by Kapitza, both for the factor β and the change in resistance.

In attempting to compare the results obtained for different metals it is very unfortunate that the work was carried out on specimens which had been strained by winding, since this only served to introduce an additional complication apart from that due to the variation in purity. It was found by Kapitza that for the metals of any one group of the periodic table, the value of β at a given temperature generally diminishes with increasing

* With larger percentages of impurity the value of β is affected.

atomic weight, as will readily be seen in Table X. In every case, except that of gold and mercury, the value of β increases on passing from a univalent element to the divalent element which follows it, but the values of β are so much affected by temperature that the true relations are not likely to be discovered until the data are sufficient to enable a comparison to be made at corresponding temperatures.

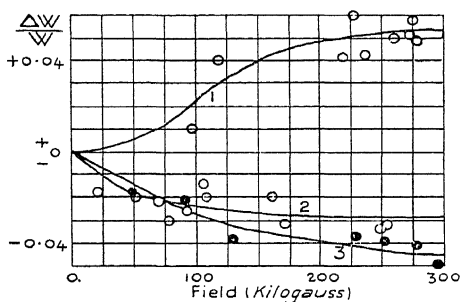
TABLE X. *Transverse Effect in the Second Group of Elements.*

Element.	Room Temperature.		193° Abs. Temperature of CO ₂ and Ether.		85° Abs. Temperature of Liquid Nitrogen.	
	$\frac{\Delta W}{W_0}$ at 300 k.gauss	$\beta \times 10^6$	$\frac{\Delta W}{W_0}$ at 300 k.gauss	$\beta \times 10^6$	$\frac{\Delta W}{W_0}$ at 300 k.gauss	$\beta \times 10^6$
Beryllium	0.65	3.1	—	—	2.3	10.3
Magnesium	0.17	0.9	0.32	1.54	2.84	12.3
Zinc	0.06	—	0.12	0.56	0.91	4.02
Cadmium	0.08	—	0.19	0.73	0.93	3.47
Mercury	—	—	0.02	—	0.05	0.5

$\frac{\Delta W}{W_0}$ shows the relative change in resistance in a transverse field of 300 kilogauss, whilst β is the constant in the equations on p. 30.

The ferro-magnetic metals iron and nickel behave quite abnormally, and in each case the change of resistance in a transverse field is very small, the variation with field strength being of the kind shown in Fig. 10. Nickel is remarkable in being the only metal in which the resistance is diminished by a transverse field.

It is, however, when we come to the borderline metals antimony and bismuth that the greatest changes are produced by a transverse field, and the effect is particularly marked in the case of bismuth, for which the phenomenon has

FIG. 10. Iron and Nickel $II \perp I$.

Curve 1—Iron. Temperature of liquid air.
Curve 2—Nickel. Temperature of liquid air.
Curve 3—Nickel. Room temperature.

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been investigated by many workers. In this case the change in resistance becomes very much greater at low temperatures, as can be seen from Table XI, which is taken from the pioneer work of Dewar and Fleming.² The full details of the process are, however, only apparent when single crystals of bismuth are investigated, and the most accurate work is again due to Kapitza.³

TABLE XI. *Transverse Effect for Bismuth.*

<i>Field Strength.</i>	<i>Specific Resistance (C.G.S. units).</i>	
	<i>Temp. 19° C.</i>	<i>Temp. - 185° C.</i>
0	116,200	41,000
8,800	149,200	738,000
21,800	257,000	6,190,000

In this table the specific resistance is expressed in C.G.S. units, and the figures can be converted into ohms by dividing by 10^9 .

With single crystals of bismuth the effect of a transverse field depends not only upon the temperature and field strength, but upon the direction of the current and the magnetic field relative to the crystal axes. In all cases, however, the change in resistance is proportional to the square of the field strength in weak fields, and follows a linear law in strong fields, so that the curves are again of the forms shown in Fig. 9. In agreement with previous workers, Kapitza found that the resistance varied with the orientation in agreement with the symmetry relations of Voigt (see p. 7), and he then showed that for the change of resistance in a transverse field, the linear portion of the curve was independent of the orientation of the crystal in the magnetic field, but that the orientation affected the constant of the square law representing the lower portion of the curve. It was also found that imperfections in the crystal lattice caused by internal stresses, cracks, &c., had no effect upon the constants of the linear and square laws, but that they affected the value of the critical field strength at which the variation changed from the one type to the other. These results were again explained on the assumption of an ideal resistance varying linearly with the magnetic field, and additional resistances caused by impurities and imperfections in the lattice.

2. *The Hall Effect.* Referring to the previous figure showing the passage of a current along a rectangular conductor, the

presence of a transverse magnetic field also causes a difference in potential to be generated between the sides of the conducting plate. The result of this is that points on the plate which, in the absence of a magnetic field, were at the same potential, find themselves at different potentials when the magnetic field is applied, so that the lines of flow of the current are altered. This is known as the *Hall Effect*, and the Hall Coefficient r is defined by the relation

where E is transverse potential difference, d the thickness of the plate parallel to the magnetic field of strength H , and I the total

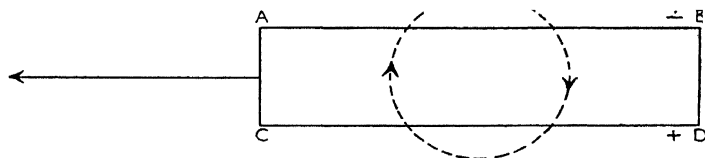


FIG. 11.

current. By convention the coefficient is taken as *positive* if the electric potential is raised on that side of the plate on which the Ampèrean current generating the magnetic field has the same direction as the current I .

Thus if $ABCD$ is the plate, and the current flows down the plate from BD to AC , then if the dotted circle shows the direction of the Ampèrean current generating the magnetic field, the Hall coefficient is positive if the potential of the side CD be raised. In the case of cubic crystals of copper it has been shown by Wold⁴ that the Hall Coefficient is independent of direction, and this has been confirmed by Jones⁵ for cubic crystals of aluminium, but with bismuth the coefficients obey the symmetry relations of Voigt (see p. 7).

As with the Transverse Effect, the magnitude of the Hall Effect is usually comparatively slight, the coefficient being positive for the metals shown in the first column of the following table, and negative for those in the second.

Positive Hall Coefficient.

Iron
Cobalt
Zinc
Cadmium
Thallium

Negative Hall Coefficient.

Copper
Silver
Gold
Nickel
Aluminium

Positive Hall Coefficient.

Tin
Lead
Iridium
Arsenic
Antimony
Tellurium
Molybdenum
Tantalum
Tungsten
Silicon
Cerium

Negative Hall Coefficient.

Indium
Lithium
Sodium
Palladium
Platinum
Bismuth
Selenium

Except for the fact that the univalent metals give negative coefficients, there does not seem to be any general connexion between the sign of the effect and the position of the element in the periodic table. For the majority of the metals the values of the coefficient are small, and lie between 10^{-3} and 10^{-6} . The values vary with the temperature and with the field strength, but these variations do not permit of any useful generalization. The effect is greater for silicon, tellurium, antimony, and bismuth, and is specially marked for the last named, for which the value of the coefficient is under some conditions as large as 10^{+2} . A very great deal of work has been carried out on this metal, and with single crystals it has been shown that the coefficient is positive when the axis of the crystal is parallel to the field, and negative when it is at right angles, the effect for the polycrystalline metal being due to the combination of the two. The concentration of attention on the Hall Effect in bismuth is distinctly unfortunate, as the metal is essentially an abnormal one, both physically and chemically, and if more of the work had been confined to the normal metals, it would have been far more likely to lead to an understanding of the fundamentals.

A few typical results are shown in Table XII from which it will be seen that for the normal metals the coefficient is only slightly affected by temperature or by the strength of the magnetic field up to 12,000 gauss. With the magnetic metals such as nickel the results are much more complex, owing presumably to the magnetic and other polymorphic changes which the metals undergo.

This table also shows the relatively enormous magnitude of the effect of bismuth, and the peculiar behaviour of the single crystals in which at low temperatures the Hall Coefficient is positive in both directions, whilst at ordinary temperatures it

is positive when the axis of the crystal is parallel to the magnetic field, and negative when at right angles.

TABLE XII. *Values for the Hall Coefficient.*

<i>Metal.</i>	<i>Field Strength.</i>	<i>Temperature.</i>	<i>Coefficient.</i>
Silver . .	7,260 gauss	- 258.4° C.	- 995 $\times 10^{-6}$
	9,065 "	"	- 991 "
	10,270 "	"	- 985 "
	7,260 "	+ 17° C.	- 801 "
	9,065 "	"	- 798 "
	10,270 "	"	- 795 "
Copper . .	7,260 "	- 258.5° C.	- 660 "
	9,065 "	"	- 655 "
	10,270 "	"	- 654 "
	7,260 "	+ 17° C.	- 495 "
	9,065 "	"	- 487 "
	10,270 "	"	- 495 "
Gold . .	7,730 "	- 258.5° C.	- 978 "
	9,500 "	"	- 971 "
	12,220 "	"	- 982 "
	7,730 "	+ 17° C.	- 727 "
	9,500 "	"	- 711 "
	12,220 "	"	- 725 "
	4,790 "	+ 840° C.	- 750 "
Bismuth .	2,060 "	- 258.4° C.	- 81.3 $\times 1.0$
	7,160 "	"	- 71.1 "
	12,090 "	"	- 67.7 "
	2,060 "	+ 17° C.	- 9.08 "
	7,160 "	"	- 6.44 "
	12,090 "	"	- 5.19 "
Bismuth Single Crystals			
to Magnetic Field	5,680 "	- 252.7° C.	+ 2.7 "
⊥ " "	5,800 "	"	+ 5.79 "
" "	5,680 "	+ 17° C.	+ 0.072 "
⊥ " "	5,870 "	+ 17° C.	- 6.58 "

3. *The Ettinghausen Effect.* At the same time, when a current flows down a flat plate, the presence of a transverse magnetic field causes a difference of temperature between the edges of the plate,

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this phenomenon being known as the *Ettinghausen Effect*. The Hall and Ettinghausen Effects are in some ways analogous, the one corresponding to a difference in electrical potential, and the other to a difference in thermal potential between the two sides of the plate. The Ettinghausen coefficient p is defined by the relation

$$\Delta\theta d$$

where $\Delta\theta$ is the temperature difference between the sides of the plate, and d , I , and H have their previous meaning. By conven-

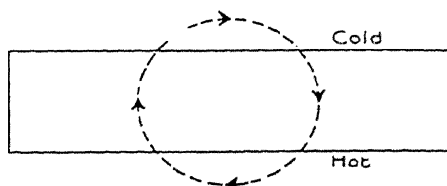


FIG. 12.

tion it is again positive if the temperature of the plate be raised on the side on which the Ampèrean current generating the magnetic field has the same direction as the electric current flowing down the plate.

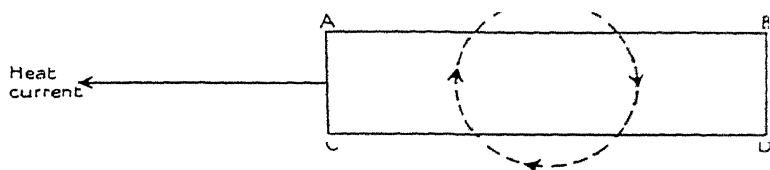


FIG. 13.

The magnitude of this effect is extremely small, and for the majority of the metals the coefficient p is of the order 10^{-7} to 10^{-9} . The coefficient is sometimes positive, and sometimes negative, but no very obvious rule appears to be followed in this respect, the Ettinghausen and Hall Coefficients having the same sign for some metals and different signs for others.

Like the Hall Effect, the Ettinghausen Effect is particularly marked in the case of bismuth, and to a lesser extent in antimony, tellurium, and silicon. For bismuth the value of p is of the order 10^{-4} to 10^{-5} and the coefficient is positive.

The Hall and Ettinghausen Effects are thus produced when an electric current flows down a conductor in the presence of a

transverse magnetic field, and the effects are produced in a plane at right angles to the current and at right angles to the magnetic field. Two exactly similar effects are met with if, instead of an electric current, a current of heat flows down a metal plate. If we again consider a flat plate with a current of heat flowing from BD to AC , the presence of a magnetic field causes a difference of electric potential between the sides AB and CD . This is known as the *Nernst Effect*, and the Nernst coefficient Q is defined by the relation

$$Q = \frac{Ed}{H} \cdot \frac{K}{\omega}$$

where E , d , and H have their previous meanings, while K is the thermal conductivity and ω the total amount of heat flowing through the cross-section of the plate per second. The same convention applies as to the sign of the coefficient. The values of Q are usually small, and are of the order 10^{-3} to 10^{-6} for most metals, but are again abnormally high for bismuth, antimony, tellurium, and silicon. For bismuth the value of Q is of the order 1 to 10^{-1} and is positive, but there seems to be no general relation between the sign of the Nernst coefficients and those of the Hall and Ettinghausen effects.

Just as the Nernst Effect is analogous to the Hall Effect, but with a current of heat replacing one of electricity, so the Ettinghausen phenomenon has a corresponding effect known as the *Righi-Leduc Effect*. In this case, when a current of heat flows down a plate in the presence of a transverse magnetic field, a difference of temperature between the two sides of the plate is observed. The Righi-Leduc coefficient S is defined by the relation

$$S = \frac{\Delta\theta}{H} \cdot \frac{d}{\omega} \cdot \frac{K}{\omega}$$

where all the symbols have their previous meanings, and where the sign of the coefficient is determined as before. The Righi-Leduc coefficients are of the order 10^{-7} to 10^{-8} for most metals, and are again higher for the same four abnormal metals, rising to about 10^{-5} to 10^{-6} for bismuth. The sign of the coefficient is different for different metals, but again no generalization appears possible in this connexion.

B. The Effect of a Longitudinal Magnetic Field.

The phenomena previously described all refer to the effects of transverse magnetic fields, but the resistance of a metal is also

affected by a longitudinal or parallel magnetic field, i.e. by a field which is parallel to the direction of the current. In all cases the resistance is increased, but for nearly all metals the effect of a longitudinal field is less than that of a transverse field. The phenomenon has only been examined for high field strengths by Kapitza,¹ who investigated the effect in copper, cadmium, aluminium, gallium, and molybdenum, and showed that the change in resistance varies with the field strength in the same way as for the transverse effect, i.e. $\frac{\Delta W}{W}$ is proportional to the square of the

field strength in weak fields, but follows a linear relation in strong fields. The linear portion of the curve has, however, a smaller slope β , and a larger critical field H_k than for the transverse effect.

The ferro-magnetic metals iron and nickel again behave abnormally, the resistance increasing in a longitudinal field until a practically constant value is reached.

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II

THE ELECTRICAL CONDUCTIVITY OF PRIMARY METALLIC SOLID SOLUTIONS

1. General Characteristics	39
2. Relative Effects of Different Metals upon the electrical resistance of solid solutions	42
3. The Effect of prolonged annealing on the Resistance of some primary solid solutions	46
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1. General Characteristics

IN the present chapter we shall deal with the electrical conductivity of primary metallic solid solutions, which we have already defined as those solid solutions in which the crystal structure of the parent metal is retained. For simplicity we shall in general confine our attention to binary alloys, since the ternary alloys, while naturally giving very much more complex results, have contributed but little to our understanding of the fundamental principles involved.

The outstanding characteristic of the electrical conductivity of primary solid solutions is that the conductivity of a pure metal is very greatly lowered by the addition of a second metal with which it forms a solid solution. As a typical example of this kind we may take the case of the alloys of silver and gold in which the two metals are completely miscible in the solid state, and form a continuous substitutional solid solution from 100% silver to 100% gold. The specific conductivities of these alloys are plotted graphically in Fig. 14.

Some little confusion arises in the presentation of results of this kind, for the specific conductivity or resistance of an alloy refers to the volume of the alloy, whilst the composition of an alloy is usually expressed in weight percentages. For some purposes the relations are shown more clearly if the alloys are dealt with in percentages by volume, and this has been done in the curve, shown in Fig. 14, which is taken from the pioneer work of Matthiessen,¹ the values having been recalculated by Guertler. This kind of relation is quite typical, and in all cases the first small additions of the second metal produce a much greater

lowering of the conductivity, or increase in resistance, than later additions.

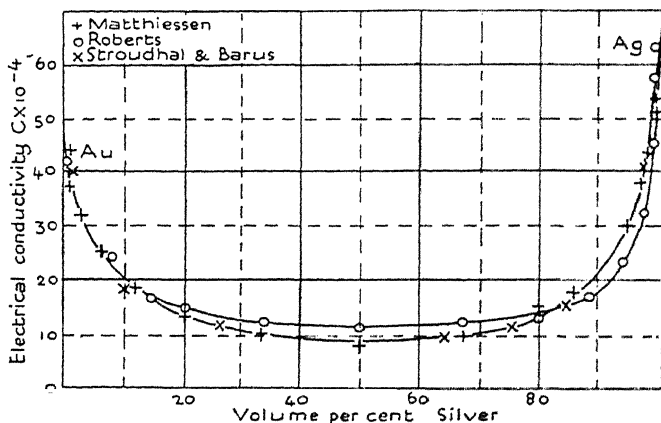


FIG. 14. The electrical conductivity of gold-silver alloys.

TABLE XIII

<i>Wt % Zn.</i>	<i>Specific Conductivity</i>
0	63.1
0.71	54.56
1.56	46.88
3.07	42.16
5.51	33.22
9.08	27.49
18.02	21.00
20.29	19.75
22.71	18.44
28.16	17.16
34.23	15.87
40.28	17.27
42.55	18.84
45.19	21.22

In the case of alloys in which the primary solid solution is of limited extent, the same general type of relation holds. Table XIII and Fig. 15 illustrate this for the alloys of copper and zinc (the α brasses), the values being taken from the work of Haas² recalculated by Guertler. In this case, at room temperatures, alloys containing up to about 35% of zinc consist of a primary solid solution of zinc in copper, the so-called α solid solution, giving rise to the α brasses. Beyond about 35% of zinc, a second solid solution makes its appearance, and the alloys contain two phases

($\alpha\beta$ brasses). This is shown by the break in the conductivity-composition curve, but as in the present book we are dealing only with the properties of single phases, we shall not deal with the two-phase region.

Relations of this type are quite general, although in some cases the conductivity-composition curves are not as symmetrical as those shown in Fig. 14 (p. 40). It is only natural that attempts should have been made to see whether the conductivity or resistance curves of the usual type can be expressed by any general formulae, but the equations suggested in this connexion are purely empirical, although in some cases they cover the facts fairly satisfactorily.

We may in the first place assume a hypothetical specific resistance of an alloy which can be calculated from the resistances of the pure metals by the simple law of mixtures, the constituents being expressed in volume percentages. If W_m be this hypothetical specific resistance, then the curve connecting W_m with the volume percentage composition will be a straight line. The actual specific resistance (W) of a primary solid solution is of course much greater than W_m , as can readily be seen from the figures given above. We may therefore take $(W - W_m)$ as a measure of the additional resistance caused by the formation of the primary solid solution, and we may denote this by W_a where

$$W_a = W - W_m.$$

The first empirical relation put forward was due to Guertler, and may be expressed in the form

$$W_a = C(100 - C) \times A,$$

where C and $(100 - C)$ are the volume percentages of the two constituents, and A is a constant.

This relation does not hold for very dilute solid solutions in which only a small amount of a second metal is present, but in

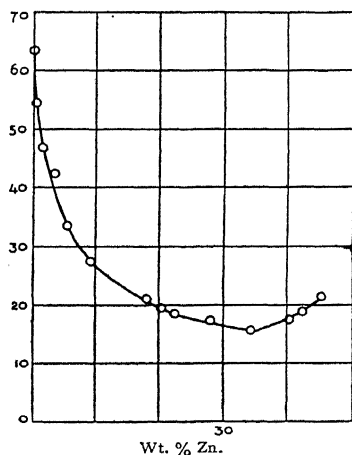


FIG. 15.

some cases it holds approximately for alloys of intermediate composition.

But this relation is of course purely empirical and is not always satisfactory, so that others have been suggested. The following equation was given by Benedicks, and covers the facts fairly well in some cases:

where a and b are constants, and n is the atomic concentration.

We shall discuss later (p. 48) a possible cause of the unsymmetrical conductivity-composition curves found with some alloys.

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2. Haas. *Ann. d. Phys.* 1894, **52**, 673.

2. Relative Effects of Different Metals upon the Electrical Resistance of Solid Solutions

Of much greater interest than these attempts to express the conductivity or resistance curves by empirical relations is the question of the relative effects produced by different metals in raising the resistance of a given metal when a primary solid solution is formed. Unfortunately very great difficulty is met with in approaching this problem owing to the great difference in the purity of the materials used by the different experimenters, and in the relative accuracy of their work. The question has been discussed by Norbury,¹ whose work has led to the discovery of some interesting relations.

To a first approximation, the increase in resistance caused by the first small additions of a solute element to a solvent metal varies linearly with the volume concentration of the added element, and this variation is very nearly independent of temperature. This last fact is very remarkable and is shown in Fig. 16, the values being taken from the work of Clay.² From this it will be seen that at temperatures between 0° and -253° C. the resistance-concentration curves are almost exactly parallel for these very dilute solid solutions.

As a standard of comparison Norbury takes the additional resistance caused by one atomic per cent. of various metals when they form a solid solution with a common solvent, and typical

results of this kind are shown in Table XIV, and are plotted graphically in Fig. 17, the data referring to solid solutions in copper, silver, and gold. The general conclusion drawn from these figures is that the additional resistance caused by one atomic per cent. of a metal increases with the distance both horizontal and vertical which separates the solute and solvent in the Periodic Table of the elements. Thus with copper, the least additional resistance occurs with the metals silver and gold, which are in the same group. Magnesium, zinc, and cadmium in Group II come next, aluminium in Group III produces a larger effect, whilst with tin and silicon in Group IV, and arsenic and antimony in Group V, the increase is even greater. On going backwards from copper to the elements of Group VIII, and VII A

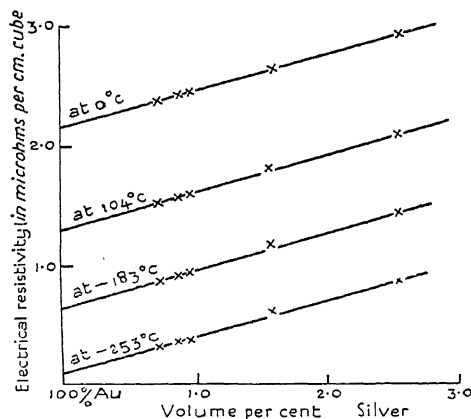


FIG. 16. Electrical resistivity of dilute solid solutions on silver in gold.

(manganese), and VI A (chromium) the effect is not so clear except that a sudden jump occurs between nickel and cobalt. A somewhat similar effect is caused by the vertical distance in the Periodic Table. Thus with copper, gold has a greater effect than silver, whilst magnesium has a greater effect than zinc. Similarly with gold, copper has a greater effect than silver, and zinc a greater effect than mercury. There are occasional exceptions to these rules, but the general tendency is nevertheless clear.

When iron is used as the solvent metal, the relative effects of the metals of its own group, nickel and cobalt, are very much

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less than those of other metals, but exact data are difficult to obtain here as it is not easy to prepare these alloys in a pure condition.

TABLE XIV. *The Effect of Various Elements on the Electrical Resistance of Solid Solutions in Copper, Silver, and Gold.*

Solute Element.	Increase in Resistance (in microhms per the presence of 1% solute element in sol		
	COPPER.	SILVER.	GOLD.
Copper . .	0	0.1 -0.5	0.35-0.74
Silver . .	0.13-0.22	0	0.2 -0.36
Gold . .	0.5 -0.65	0.3 -0.6	0
Magnesium .	0.8	0.8 -1.3	—
Zinc . .	0.26-0.31	0.5	0.85-0.95
Cadmium .	—	0.4	0.35-0.64
Mercury .	—	—	0.4
Aluminium .	0.8 -1.1	1.6 -2.0	—
Silicon . .	3.0 -3.3	—	—
Tin . .	2.6	4.0 -5.0	7.5
Arsenic . .	5.3 -5.6	—	—
Antimony .	5.5 -7.5	—	—
Nickel . .	1.1 -1.2	—	—
Cobalt . .	2.5 -3.5	—	—
Iron . .	—	—	4.0 -6.0
Manganese .	2.9 -3.0	—	—
Chromium .	4.0	—	—
Palladium .	—	0.4	—
Platinum .	—	0.7 -1.5	0.8

—Alternative figures are given where the results of different workers do not agree.

There is, however, no doubt that, as far as the data go at present, the increase in resistance is very much less when the solvent and solute metals are separated only by one or two places in the Periodic Table, and that in the case of copper, silver, and gold these effects are much more clear when one deals with metals to the right of the transition elements* than when one goes to the left.

It has been suggested by some writers that since the specific resistance involves the volume of the test piece, the above method of comparison is not really justified, and that strictly speaking

* We are here assuming the Periodic Table to be in its usual form, and that magnesium and aluminium correspond to the *B* group and not the *A* group metals.

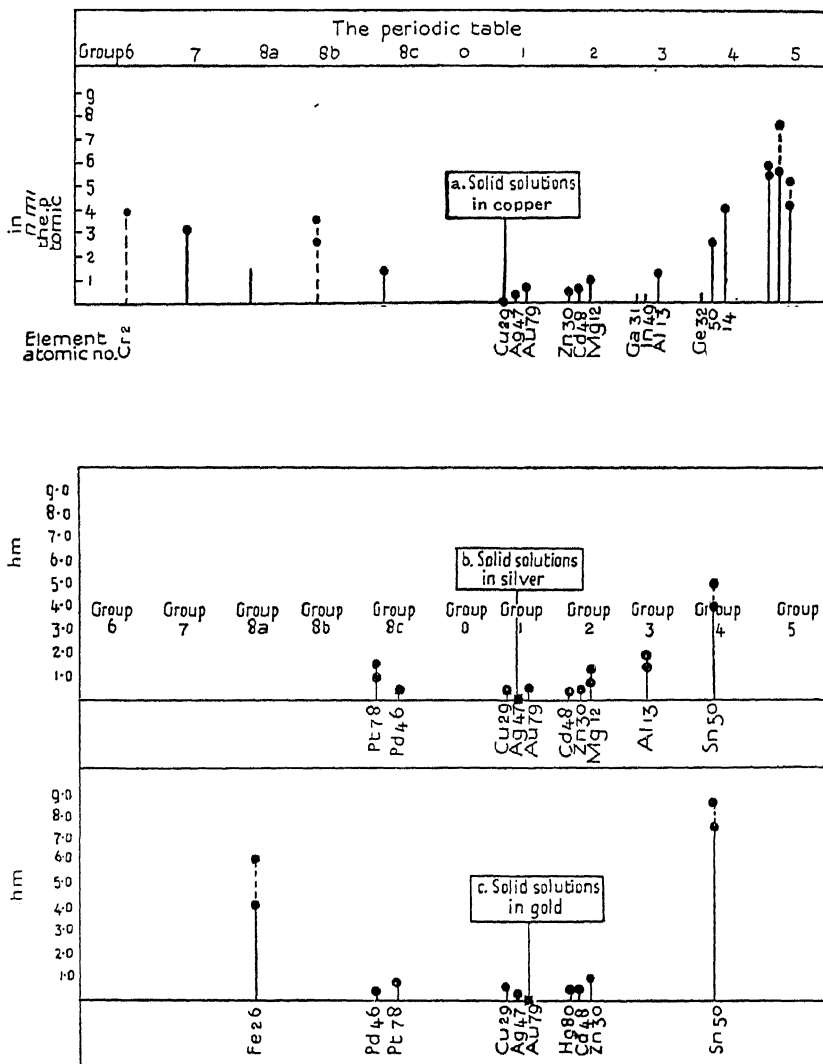


Fig. 17. Relative increase in resistance caused by one atomic per cent. of various metals in solid solution in copper, silver, and gold

the comparison should be between volumes of metals containing equal numbers of atoms. With a given solvent, however, the densities of very dilute solid solutions are so nearly the same that the general conclusions reached above are not invalidated, although when one comes to compare the effect of a given solute in different solvent metals the point becomes much more important. Up to the present, however, no very general relations have been discovered as to the relative effect of metals in solid solution in different solvents, and in view of the complex nature of metallic conduction this is really only to be expected.

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3. The Effect of Prolonged Annealing on the Resistance of some Solid Solutions

The phenomena which we have described above, and, in particular, the conductivity-composition curves shown in Fig. 14, refer to primary metallic solid solutions in the ordinary annealed condition, in which the alloys are usually described as 'homogeneous'; in this state solid solutions such as those of copper and gold are of the substitutional type, and the two kinds of atoms are arranged at random on a common lattice. When, however, such alloys are subjected to prolonged annealing it is found that for alloys of certain compositions a marked increase in conductivity sometimes occurs. These changes have been studied in detail by Johansson and Linde,¹ who have shown that this change in conductivity is accompanied by a rearrangement of the atoms in the lattice. For example, in the case of the alloys of copper with gold, palladium, or platinum, alloys containing 75 atomic per cent. of copper consist, after a short annealing to render them homogeneous, of the two kinds of atoms arranged at random on a face-centred cubic lattice. But after prolonged annealing the atoms rearrange themselves so that the atoms at the centres of the cube faces are copper, whilst those at the cube corners are of the other metal. In the same way with the 50 atomic per cent. alloy containing equal numbers of the two kinds of atoms, prolonged annealing causes a rearrangement of the atoms with a marked decrease in resistance, although the resulting structures are not always the same. The CuAu alloy becomes tetra-

gonal, and the CuPd alloy trigonal, but in each case the change is essentially one in which the two kinds of atoms take up definite positions on the original face-centred cubic lattice, instead of being situated at random on this lattice. On the other hand in the case of CuPd the change is more drastic, and the structure becomes body-centred cubic of the caesium chloride type. On heating at a sufficiently high temperature, these regular structures are destroyed, and the alloy again becomes a simple solid solution with the two kinds of atoms arranged at random on a common face-centred cubic lattice. With sufficiently slow heating or cooling the change from the ordered to the disordered state can be detected by the ordinary method of thermal arrests (heating or cooling curves), so that we have what may really be changes from one phase to another, although marked hysteresis effects are shown. According to Borelius, Johansson, and Linde, in the cases of Cu_3Au , Cu_3Pd , and CuAu , the changes from the ordered to the disordered

state can be considered simply as a disturbance of a *homogeneous* equilibrium, in which the atoms rearrange themselves on the original lattice, whereas the more drastic change in the case of CuPd involves a *heterogeneous* equilibrium. These effects are illustrated diagrammatically in the accompanying figure, and

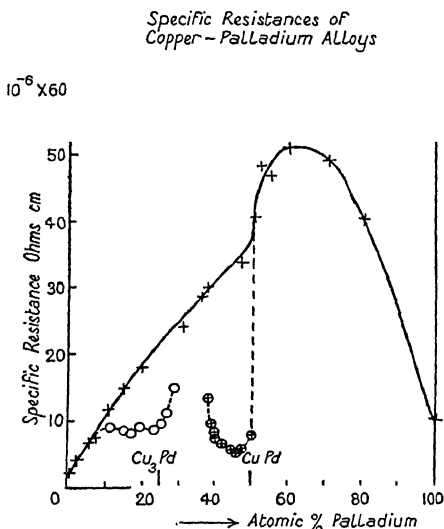


FIG. 17 A.

To illustrate the effect of prolonged annealing at a low temperature on the resistance of copper-palladium alloys. The points marked + indicate the specific resistances of specimens which were annealed for 2-3 hours, just below the melting-point, and then quenched. In this state the two kinds of atoms are arranged at random on a face-centred cubic lattice. The points marked O and ⊕ refer to specimens after prolonged annealing below 400° C. In these alloys atomic rearrangement has partly or completely taken place, the points marked ⊕ giving evidence of a body-centred cubic structure, whilst in those marked O the structure is face-centred cubic, but the X-ray diffraction patterns contain additional lines indicating that the copper atoms occupy the centres, and the palladium atoms the corners of the unit cube.

have naturally given rise to the question whether all simple solid solutions will undergo similar changes. According to Johansson and Linde in the silver-gold alloys, which form a complete series of solid solutions, the atoms always maintain a haphazard arrangement on a common lattice, and it seems probable that the tendency for the atomic rearrangement to take place is increased by increasing difference in the sizes of the two atoms, since the atomic radii of silver and gold are nearly the same, but are greater than that of palladium. Whether such changes involve the formation of a definite compound or not is at present undecided, for, as we have already explained in our Introduction, chemical combination in the usually accepted sense of the word involves more than a mere symmetrical arrangement of atoms in a solid, and these interesting phases may be what we have defined as symmetrical solid solutions rather than true compounds.

These phenomena should make it apparent that the electrical conductivity of a solid solution is in some ways rather a dangerous quantity on which to base arguments, unless the structures of the alloys are carefully checked by X-ray measurements. For even a short annealing at a low temperature, or an insufficiently rapid quenching from a high temperature, may produce a partial rearrangement, in which case the conductivity has little fundamental value. It will be noticed, for example, that the minimum resistance of the copper-palladium alloys shown in the figure does not occur at the exact equi-atomic composition, and this may be due to insufficient annealing.

Where two metals form a complete series of solid solutions it is probable that there is always a tendency to take up an ordered structure on prolonged annealing at a low temperature, although if the atomic volumes are nearly the same, the tendency may be very slight. But the work of Johansson and Linde seems to indicate that a complete rearrangement of atoms only occurs at certain simple whole-number ratios. At present our knowledge of these interesting changes is in its infancy, but it may be emphasized that they do not in any way affect the general rule that the resistance of a pure metal is greatly increased by the presence of small quantities of a second metal in solid solution. We may, however, suggest that the fact that in some cases the conductivity-composition curves do not have the typical symmetrical form shown in Fig. 14 (p. 40) may be due to changes such as those described by Johansson and Linde

having taken place to some extent during the annealing of the specimens.

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See also: Borelius, Johansson, and Linde. *Ann. Physik*, 1928, 86, 291;
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4. Temperature Effects and the Temperature Coefficient of Resistance

The marked decrease in the conductivity of a pure metal, which is observed when a second metal is present in solid solution, is accompanied by a corresponding decrease in the temperature coefficient, and in general it may be said that the composition-conductivity, and composition-temperature coefficient curves are roughly parallel. In other words, whilst the formation of a primary solid solution greatly lowers the conductivity of a pure metal, it makes the conductivity much less dependent upon temperature. It is for this reason that the temperature coefficient of a metal is so often a useful indication of its purity, for, unlike the specific resistance, the temperature coefficient of a given sample of metal is not affected by the presence of holes or other internal defects.

The general type of composition-temperature coefficient curves is that shown before in Fig. 14 (p. 40), but the extent to which the temperature coefficient is lowered varies greatly from one case to another. Thus for copper-cobalt alloys, which form a continuous series of solid solutions, the minimum temperature coefficient is about 0.0008 according to the values given in Landolt's tables of Physical Constants, but in the case of the copper-nickel alloys, which also form a continuous solid solution, the alloy containing 60% of copper and 40% of nickel has a mean temperature coefficient between 0° and 100°, of only 0.0001, and this coefficient becomes practically zero from between 300° and 400° C. This alloy formed the original 'Constantan' which was so useful for electrical instruments in order to avoid errors due to fluctuations in room temperatures. The old 'Constantan' alloy has, however, been modified by the addition of small amounts of manganese and iron, and in this form its temperature coefficient changes sign between 0° and 25°, so that it is better suited for use at room temperature than the original alloy for which the temperature coefficient vanished between 300° and 400° C.

At very low temperatures the resistance of solid solutions diminishes, but not to the same extent as that of pure metals. Thus at -189° C. the value of $\frac{W_{\theta}}{W_0}$ for Constantan is, according to Niccolai, 0.9654, whilst the same worker's values for the pure metals copper and nickel were 0.191 and 0.182 respectively, so that the change is very much less for the solid solution. Where appreciable quantities of one metal are dissolved in another in solid solution, supra-conductivity is not shown, but for very dilute solid solutions the position is more obscure.

Until recently it was always thought that no solid solutions could show supra-conductivity, but in the last few years evidence has been accumulated that a supra-conducting metal can take up small quantities of a second metal into solid solution and still remain supra-conducting. Unfortunately the alloys examined have in several cases been of a very unsuitable nature, so that the whole subject is in a most confused state.

It was found by McLennan, Wilhelm, and Niven¹ that additions of cadmium to lead in quantities up to 5% do not destroy the supra-conductivity, although the exact form of the temperature-resistance curves is altered. The equilibrium diagram of the system cadmium-lead indicates that slight solid solutions are formed, but the specimens used in this work were prepared by simply cooling the molten alloy, and no annealing treatment was given. Under these conditions the alloys will have a 'cored' structure of lead-rich dendrites surrounded by a matrix relatively more rich in cadmium, so that the whole structure is very confused, and the results lose much of their fundamental significance, although they suggest that small quantities of cadmium in solution in lead may not destroy the supra-conductivity.

More recently, de Haas, van Aubel, and Voogd² have examined the behaviour of eutectic mixtures of two supra-conducting metals which form slight solid solutions in each other, and also eutectics of two metals only one of which shows supra-conductivity. The results obtained are very confusing, and it is indeed unfortunate that attention should have been concentrated on eutectic alloys, since microscopic work shows that these have highly complex micro-structures* which can only serve to com-

* In particular the relative amount of inter-crystalline material is enormously greater in eutectic structures than in other cases. Recent work in connexion with aluminium alloys has also shown that if super-cooling occurs during the solidification of a eutectic, the composition of

PLICATE the results. The bismuth-tin and cadmium-thallium eutectics become supra-conducting at a higher temperature than the corresponding pure supra-conductors tin and thallium. This appears a very remarkable phenomenon, especially as the supra-conductivity still appears sharply.

On the other hand, in the tin-zinc and tin-cadmium eutectic alloys the supra-conductivity appears at a lower temperature than with the pure metals, although the change is still sharp. But with the gold-thallium eutectic the temperature at which supra-conductivity occurs is considerably depressed, and the change is much more gradual. Supra-conductivity was also obtained in some lead eutectics, so that the general conclusion is that a small amount of a second metal in solid solution does not necessarily destroy the supra-conductivity.

The most surprising result obtained by de Haas, van Aubel, and Voogd³ was, however, that a eutectic alloy of bismuth and gold becomes supra-conducting at 1.915° Abs. in spite of the fact that neither metal in the pure state is a supra-conductor. By working with alloys of different compositions⁴ they conclude that the constituent responsible for the supra-conductivity is a solid solution of bismuth in gold which, according to the equilibrium diagram, should contain about 4% bismuth. The whole subject is thus in a very uncertain condition, and there is much scope for further work, but it is to be hoped that this will be carried out on well-annealed alloys which consist of simple solid solutions, for the use of complex eutectic structures can only serve to confuse the results.

Matthiessen's Rule.

The general similarity between the composition-conductivity, and composition-temperature coefficient curves was summarized by Matthiessen as long ago as 1864 in the so-called 'Matthiessen's Rule', which may be described as follows.

If α is the temperature coefficient of resistance of an alloy and is given by

$$\frac{\alpha}{100} = \frac{C_0 - C_{100}}{C_0} : \frac{W_{100} - W_0}{W_{100}}$$

where C and W are the specific conductivity and specific resistance respectively, and if α_m and C_m are the (hypothetical) values of the temperature coefficient and conductivity of an alloy the two phases may be quite different from that under equilibrium conditions.

calculated by the law of mixtures from the values for the pure metals, then

$$\frac{\alpha_m}{\alpha} = \frac{C_m}{C}.$$

In this equation the values of α_m and C_m are calculated from the volume composition of the alloy, and not from the weight composition. Since for most pure metals the temperature coefficient is practically constant, and, as defined above,* varies from about 27 to 31 for most metals, the above relation may be expressed in the form

$$\frac{\alpha C_m}{C} = 29 \text{ approximately.}$$

The following figures may be quoted to illustrate the validity of this law, and it will be seen that the rule holds in some cases not only for alloys consisting of a single solid solution (e.g. silver-gold) but also for alloys consisting of two phases, each of which is a solid solution, as, for example, the silver-copper alloys of intermediate composition.

TABLES XV AND XVI

<i>Gold-Silver Alloys (complete isomorphism).</i>				
<i>Composition in Volume %</i>	$C \times 10^{-4}$.	α .	$C_m \times 10^{-4}$.	$\frac{\alpha C_m}{C}$.
20.14 vol. % Ag.	12.78	10.21	38.83	31.0
47.92 "	9.37	6.71	41.72	30.6
80.14 "	13.25	8.44	45.07	29.6
<i>Copper-Silver Alloys (limited solid-solubility).</i>				
1.65 vol. % Ag.	43.88	26.50	47.10	28.0
4.83 "	40.84	25.57	47.10	29.5
53.33 "	38.60	22.75	47.11	27.7
98.47 "	47.88	26.51	47.12	26.1

The rule, however, is an approximate one only, and fails badly with alloys of some of the magnetic metals for which the values

* Apart from the factors 100 the temperature coefficient used by Matthiessen, namely $\frac{100}{W_{100} - W_0} (W_{100} - W_0)$, is slightly different from the usual coefficient $\frac{1}{W_0} \left(\frac{W_{100} - W_0}{100} \right)$. This is because Matthiessen really dealt with the temperature coefficient of conductivity instead of the more usual coefficient of resistance.

of $\frac{\alpha_m}{C}$ are much too high, whilst the law also breaks down completely in the case of those alloys such as Constantan in which the temperature coefficient becomes zero or even negative.

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2. de Haas, van Aubel, and Voogd. *Proc. K. Akad. Amsterdam*, 1929, 32, 715, 724.
3. de Haas, van Aubel, and Voogd. *Ibid.* 1929, 32, 226.
4. de Haas, van Aubel, and Voogd. *Ibid.* 1929, 32, 724.

5. Miscellaneous Effects

Effect of Pressure.

Apart from the effects of temperature and composition, very little is known of the factors affecting the resistance of primary metallic solid solutions. This is partly because the study of alloys is a comparatively recent science, and partly owing to the fact that the investigators concerned with the electrical measurements have not paid sufficient attention to the exact condition of the alloy specimens with which they have dealt.

As far as can be judged from the very fragmentary evidence available, the general rule is that metallic solid solutions are less affected by reversible factors such as temperature, pressure, &c., than pure metals.

In connexion with the effect of pressure upon resistance, it was found by Bridgman that with pure metals, in several cases, the pressure coefficient increased (numerically) with the purity of the specimen, and since the impurities are usually partly, if not completely, in solid solution, this may be taken as confirming the general principle.

The effect of pressure upon the resistance of gold-silver alloys has been determined by Beckman,¹ who found that the pressure coefficient varies with composition in much the same way as the temperature coefficient, that is to say, a marked fall in the numerical value of the pressure coefficient of resistance is caused by the first small additions of the solute metal. This is well shown in the table and figure on p. 54.

The pressures used in this work were from 0 to 2,700 atmospheres and it was found that the pressure coefficient is a linear function of the specific conductivity, so that if the specific conductivity of any alloy be plotted against the pressure coefficient, a straight line is obtained.

The Electrical Conductivity of

TABLES XVII AND XVIII

Pressure Coefficient of Resistance of Gold-Silver Alloys.

Volume % Au.	Pressure Coefficient of Resistance $a = \frac{1}{W} \frac{dW}{dp}$	Specific Conductivity C.
0.0	3.59×10^{-6}	6.45×10^5
1.9	2.41 "	4.37 "
8.4	1.6 "	2.33 "
20.5	1.26 "	1.31 "
38.0	1.16 "	0.991 "
51.2	1.15 "	0.978 "
64.2	1.13 "	1.01 "
76.6	1.20 "	1.25 "
89.7	1.48 "	2.03 "
97.9	2.22 "	3.63 "
100.0	2.78 "	4.81 "

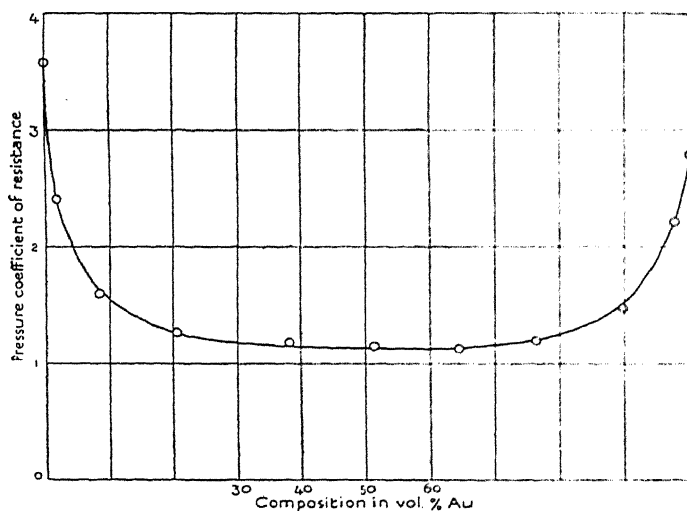


FIG. 18.

So far as is known this type of variation is quite general and the negative pressure coefficient of a normal metal is lowered *numerically* when a solid solution is formed. This may be described in another way by saying that the formation of a solid solution increases the pressure coefficient *algebraically*, and in

some cases the change is so great that the alloys of intermediate composition have positive pressure coefficients whilst their parent metals have the usual negative coefficients. This effect has been observed by Bridgman² for the alloys of iron with cobalt and nickel, but in other cases the change is not so great, and the pressure coefficient remains negative throughout when the solid solution is formed, although greatly reduced in numerical value.

Effect of Tension.

Bridgman³ has also measured the tension coefficient of specific resistance of 'manganin' and 'therlo' which are essentially copper-manganese alloys containing approximately 85% of copper with small amounts of other metals.* The values found for the tension coefficient of specific resistance were -0.6×10^{-6} for 'manganin', and -0.73×10^{-6} for 'therlo', and are thus of the same order of magnitude as those of pure metals. But systematic work on the relation between the composition and the tension coefficient does not seem to have been carried out.

Effect of Deformation.

The resistance of a primary solid solution is also affected by deformation or 'cold work', and in some cases at any rate the relative change is considerably greater than that occurring in a pure metal. Thus Guillet and Ballay⁴ found the following percentage increases in resistance caused by cold-working α brasses and bronzes of compositions stated. The percentage increase is that compared with the same wire after annealing at 650° C., all the alloys being simple solid solutions.

TABLE XIX

<i>Alloy.</i>	<i>Composition.</i>	<i>Percentage Increase in Resistance on cold-working.</i>
Pure Copper .	100 % Cu	+2.0
Brass .	91.7 % Cu 8.3 % Zn	+3.6
" .	81.8 % Cu 18.2 % Zn	+11.4
Bronze .	92.5 % Cu 7.3 % Sn	+4.1

It will be seen that the increase in resistance on cold-working is in all cases greater than that for pure copper, which is quite a

* The 'therlo' alloy used by Bridgman contained copper 85%, manganese 13%, and aluminium 2%. The composition of the 'manganin' used does not appear to be stated, but these alloys usually contain copper 82-6 %, manganese 4-15 %, nickel 2-12 %, and traces of iron.

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typical metal as regards the magnitude of the effect, but it is too early yet to be able to say whether this is a general characteristic of all primary solid solutions.

Masima and Sachs⁵ have made a detailed study of the effect of deformation upon the electrical resistance of single crystals of α brass containing about 72% of copper, when these crystals are extended by a simple tensile stress. In this work measurements were made of the change in electrical resistance, and the percentage reduction in cross-sectional area, and it was found that the curves divide themselves into three distinct parts. The first small extension of the crystal produces a considerable increase in the specific resistance of about 1%. Further extension has practically no effect upon the specific resistance until the cross-sectional area is reduced by 20 or 30%,* after which the resistance again begins to increase with increasing deformation. These results appear to indicate that when once the extension has begun the slipping occurs on one set of planes for a considerable time so that the resistance is unaffected, after which slipping occurs on a further set of planes, and the whole crystal begins to break up with increasing resistance.

From the above description it can be seen that we have but a very incomplete knowledge of the relations between the compositions of solid solutions on the one hand, and the effects of pressure, tension, deformation, magnetic fields, &c., upon their electrical conductivities, and there is much scope for further work in this connexion. It is, however, essential that this work shall be carried out on specimens which have been annealed or otherwise treated in such a way that they have reached true equilibrium. Isolated measurements on 'cast' alloys of commercial purity are of very little value from the point of view of finding out the fundamental principles involved, and every effort should be made to use pure alloys which have received a suitable treatment.

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* The exact point at which the change occurs depends upon the orientation of the crystal axis relative to the stress.

III

THE ELECTRICAL CONDUCTIVITY OF SECONDARY SOLID SOLUTIONS AND INTERMETALLIC COMPOUNDS

1. Introductory	57
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3. Secondary Solid Solutions and Compounds of Variable Composition	60

1. Introductory

IN the Introduction we defined secondary solid solutions as those solid solutions in which the crystal structures differed from those of the parent metals, but in which chemical combination, in the sense of electron transference or sharing, did not take place, whilst intermetallic compounds of fixed or variable composition were defined as phases in which definite chemical combination had occurred. As we explained before, the evidence at present is often insufficient to enable us to decide conclusively to which class a given phase belongs, and for this reason it is advisable to consider the two together.

The experimental evidence as to the electrical conductivity of such phases is unfortunately not always reliable. In the first place, the great majority of these substances are brittle, and this prevents their being drawn down to wire for the measurement of the resistance. The result of this is that the greater part of the work has had to be carried out on cast material, or on thin rods prepared by sucking the molten alloy up a glass or metal tube. Owing to the contraction occurring on solidification, specimens prepared in these ways are always liable to contain small holes or cracks, which make the measured specific resistances higher than the true values. A further difficulty is that in many cases the compounds have little or no solid solubility range, and the preparation of an alloy of the exact composition is by no means easy. This, however, is not so very serious because the conductivity of a two-phase alloy is almost a linear function of the composition, expressed in volume percentages of the constituents, and consequently a small amount of a second constituent does not cause much difference in the conductivity, and this source of error can, to a great extent, be avoided by working with a series of alloys on either side of the compound, and then interpolating to the exact composition. An additional source of error is that many of the electrical measurements were made

before it was recognized that alloys often require long annealing or other suitable treatment before they reach true equilibrium.

The measurements of the temperature coefficient of resistance are not affected by the presence of flaws in the specimen, and this is one of the great advantages of such measurements, but they are of course still affected by errors in composition, or lack of true equilibrium.

2. Intermetallic Compounds of Fixed Composition, or of very slight solid solubility range

Taken as a whole, the intermediate phases met with in binary alloys divide themselves up into those in which the compositions are fixed, or do not vary by more than one or two atomic per cent., and those in which a considerable range of solid solubility is shown. There are occasional exceptions to this rule, and the experimental evidence is at present incomplete, but taken as a whole this distinction seems to be fairly general. The substances in the first class are usually referred to as compounds, but opinion is at present divided as to whether all intermediate solid solutions involve chemical combination or not. We may therefore deal first with those intermetallic compounds of fixed or of very slightly variable composition, in which there is general agreement that a true compound is formed. In such cases the general rule appears to be that the resistance of a binary intermetallic compound of fixed composition is always greater than that of one of its constituent elements, and is nearly always greater than the resistance of either constituent element. In other words, no intermetallic compound has a higher conductivity than the better conducting of the two metals from which it is formed, but in a few cases the compound may have a higher conductivity than one of its constituent elements, particularly when one of these is a border-line metal such as antimony which is not exerting its full valency, as for example in the compound Cu_2Sb . As examples of these general rules the figures given in Table XX may be consulted.

In general it will be noticed that the specific resistance of a compound is greater when it is formed by the union of an electro-positive metal with one of the 'borderline' metals such as antimony, bismuth—or even tin and lead—which show both metallic and non-metallic properties, than when the compound is formed from two electro-positive elements. But no very general relations have been traced in this connexion. Thus the resistance of the

compound Mg_2Sn is about eight times that of Mg_2Pb , and nearly twenty times that of Cu_3As . But apart from this no very general relations appear to have been traced between the conductivity of a compound and its chemical formula. In some ways this is only to be expected, since a satisfactory comparison can hardly be made until there is some knowledge of the density of the compounds, and of their molecular weights, and at present evidence on these points is generally lacking.

TABLE XX

<i>Compound.</i>	<i>Specific Resistance.</i> $\times 10^6$	<i>Specific Resistance of Constituent Elements.</i> $\times 10^6$	<i>Temperature Coefficient of Resistance.</i>
Mg_2Pb	148.0	Mg 4.4; Pb 21.1	0.0025
Mg_2Sn	1096.0	Mg 4.4; Sn 11.6	0.0045
Mg Cu_2	5.5	Mg 4.4; Cu 1.7	0.0031
Mg_2Cu	11.9	" "	0.0037
Mg Zn_2	15.9	Mg 4.4; Zn 6.4	0.0029
Mg_3Bi_2	c. 130.0	Mg 4.4; Bi 11.4	0.0037
Mg_3Ag	16.0	Mg 4.6; Ag 1.6	0.0031
Cu_3Sn	11.12	Cu 1.7; Sn 11.6	0.0035
Cu_2Sb	8.8	Cu 1.7; Sb 3.9	
Cu_3As	59.0	Cu 1.5; As 3.5	0.0027

In contrast to the actual specific resistances, the temperature coefficients of resistance of intermetallic compounds at ordinary temperatures are often very much the same as those of pure metals. This is shown in the last column of Table XX, from which it can be seen that the temperature coefficients of the various compounds vary from 0.0025 to 0.0045, the corresponding values for pure metals varying from about 0.003 to 0.006. In some ways this is very remarkable, and it shows that the general correspondence between conductivity and temperature coefficient, which holds for primary solid solutions, breaks down entirely when a definite compound is formed. The above remarks refer to the ordinary temperature coefficients between 0°C . and 100°C ., and at present little is known of the behaviour at low temperatures. As will be appreciated later (p. 309), theoretical considerations suggest that true metallic compounds will retain positive temperature coefficients of resistance down to very low temperatures, whilst the phenomenon of minimum resistance may be expected in those compounds which are essentially ionic

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or co-valent structures, but in which electrons may be set free as the temperature is raised.

De Haas, van Aubel, and Voogd¹ have investigated the behaviour of some alloys at very low temperatures, and claim to have discovered supra-conductivity in the case of the compounds Bi_5Tl_3 , SbSn , Sb_2Sn_3 , Pb_2Au , and Sb_2Tl_3 , but unfortunately the evidence is not always conclusive. The compound Bi_5Tl_3 forms slight solid solutions but melts at constant temperature, so that a homogeneous alloy can readily be obtained, and in this case the supra-conductivity appears to be conclusively established, and is of great interest. But the remaining compounds melt with decomposition, and are formed on cooling from the liquid by peritectic reactions, which, even with very slow cooling, do not proceed to completion, so that the solid alloy has a very confused structure. Theoretically such alloys should become homogeneous on long annealing, but owing to the low melting temperatures true equilibrium can scarcely ever be obtained, and as no details are given in this connexion it is doubtful whether the specimens examined consisted of the pure compounds.

REFERENCE

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3. Secondary Solid Solutions and Intermetallic Compounds of Variable Composition

We have already indicated that the experimental evidence does not always enable us at present to distinguish between secondary solid solutions and intermetallic compounds of variable composition, and for this reason we may consider under one heading all intermediate phases of variable composition, without committing ourselves on the question of the existence of definite chemical combination.

As typical examples of these phenomena we may consider in some detail the work of Soldau on gold-zinc alloys, and that of various workers on the β phase of the copper-zinc alloys.

The alloys of gold and zinc are very complex, and the accepted equilibrium diagram is shown in Fig. 19. The exact details of this diagram need not concern us here, but the essential points are that, in addition to the primary solid solutions in gold and zinc, there is an intermediate solid solution denoted β , which ranges round the equi-atomic composition, the limits of solid

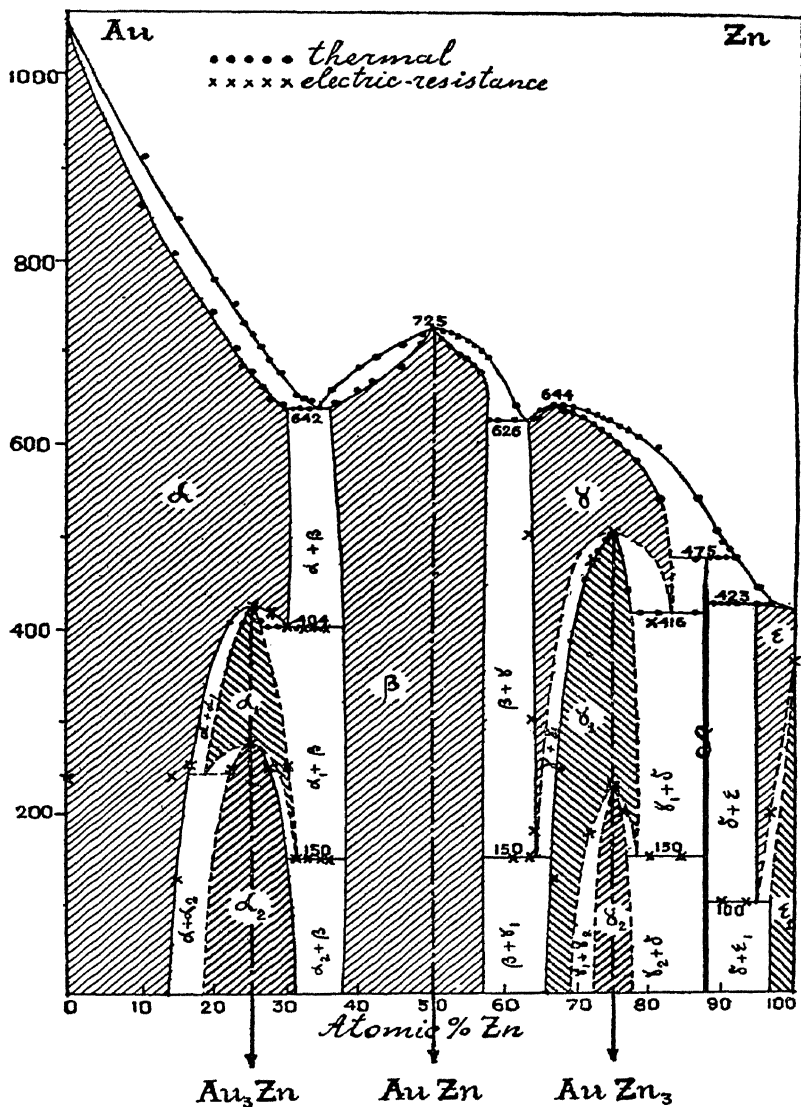


FIG. 19. Equilibrium diagram of gold-zinc alloys

α . Primary solid solution of Zn in Au

ϵ . Primary solid solution of Au in Zn

α_1 , α_2 , β , γ , γ_1 , γ_2 , intermediate phases

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solubility being from approximately 38 to 57 atomic per cent. Besides this there is an intermediate phase α_2 ranging round the composition 25 atomic per cent. zinc, the limits being from 18 to 32 atomic per cent. zinc; above about 200° C. this undergoes some kind of a phase change into a new solid solution denoted α_1 , but of much the same solid solubility limits. In addition to these intermediate solid solutions, there are three others denoted γ , γ_1 , and γ_2 , of which γ_1 and γ_2 range round the composition 75 atomic per cent. zinc, the exact limits of solid solubility being as shown in the diagram.

We have thus a system in which there are several intermediate phases of distinctly variable composition, as well as the simple primary solid solutions, in the parent metals gold and zinc. The electrical conductivity of these alloys at different temperatures has been investigated by Soldau¹ in some detail, and the results of the conductivity measurements are summarized in Fig. 20. The specimens were prepared by sucking the alloy into a narrow tube and were annealed for six days at 350° C. and then very slowly cooled to room temperature. For the conductivity measurements the specimens were then gradually heated and cooled, the conductivity being measured at intervals of 25° during both heating and cooling.

We may consider first the β phase which ranges round the equi-atomic composition, and here it will be seen that the conductivity-composition curves rise to a maximum at 50 atomic per cent. zinc. The maximum is less sharply marked as the temperature rises, but at all temperatures it occurs at exactly the same composition. At 25° C. the equi-atomic alloy has a specific conductivity of 12.92×10^4 as compared with 43.54×10^4 and 16.67×10^4 for pure gold and pure zinc respectively.

Concurrently with this maximum conductivity, the temperature coefficient of resistance—this was estimated from measurements at 0° C. and 25° C.—rises to a sharp maximum at the equi-atomic composition at which it equals 0.00334 as compared with 0.0038 and 0.0041 for the pure metals gold and zinc. The temperature coefficient of the equi-atomic alloy is thus much nearer to that of a pure metal than is the conductivity.

In exactly the same way in the case of the γ , γ_1 , and γ_2 phases, the conductivity and temperature coefficient curves rise to well-defined maxima at the exact composition AuZn_3 . In this case reference must be made to the diagram to see which phase is referred to at each different temperature.

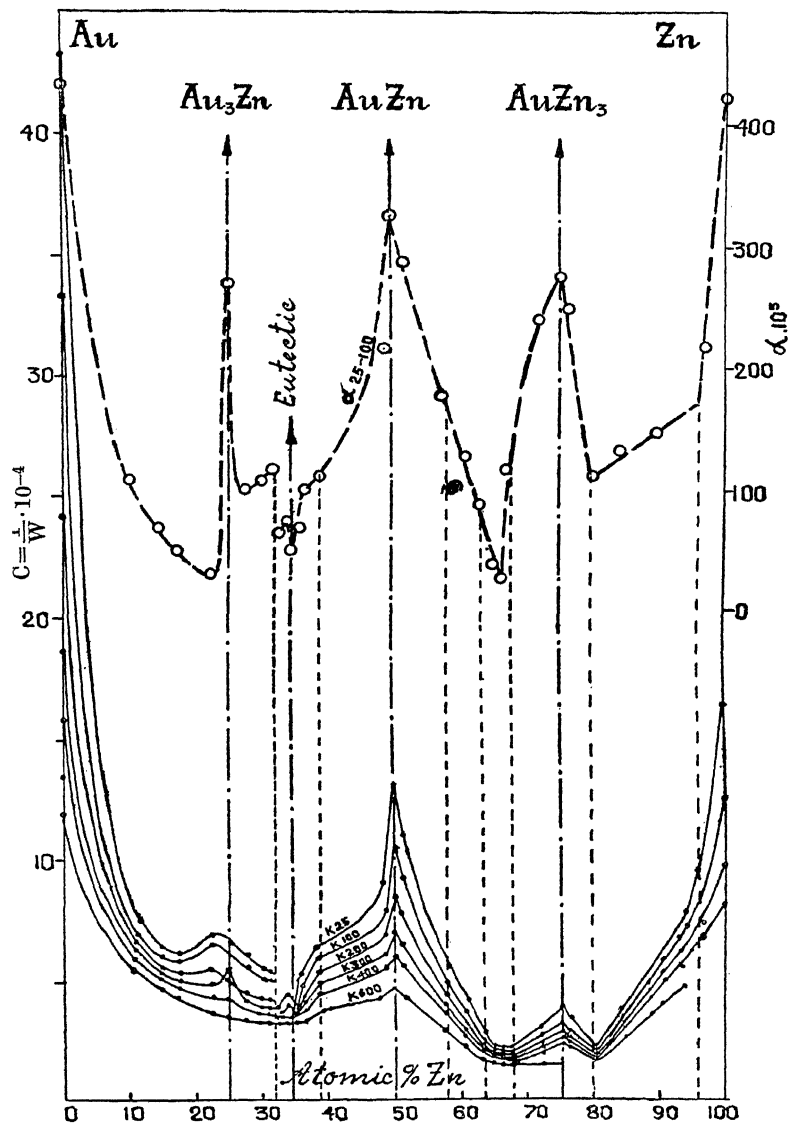


FIG. 20. Electrical Conductivities and Temperature Coefficients of gold-zinc alloys. The lower curves show the specific conductivities of the alloys at the temperatures specified. The upper curve shows the temperature coefficient determined from measurements at 25° and 100° C.

In the case of the α_1 phase exactly the same phenomenon is met with and the conductivity and temperature coefficient curves rise to a maximum at the composition Au_3Zn . On the other hand, with the α_2 phase, which is stable at the lower temperature, the maximum points on the conductivity curves are at about 23 atomic per cent. zinc, although on the temperature coefficient curve the maximum is at 25 atomic per cent.

These results were taken by Soldau as indicating that the γ , β , and α_1 phases were solid solutions in stable compounds AuZn_3 , AuZn , and Au_3Zn , but that the α_2 phase was a solid solution in a low-temperature form of Au_3Zn which decomposed on heating. This last conclusion was based on the fact that with the α_2 phase the maximum on the conductivity curves was not exactly at 25 atomic per cent. zinc, but that, by drawing rather arbitrary smooth curves through the few points obtained, it appeared to approach the composition AuZn_3 as the temperature was lowered. The evidence on this point was, however, very incomplete, as sufficient measurements were not made to determine the position of the maximum with accuracy, and the conductivity values were not in exact agreement with those for the temperature coefficients.

Relations of this kind appear to be quite general. Thus in the case of the β phase in the copper-zinc alloys (the constituent of the so-called β brasses), the conductivity curves again rise to a maximum near the equi-atomic compositions. The conductivities of these alloys have been determined by Puschin and Rjaschsky,² Matsuda,³ and by Haughton and Griffiths.⁴ In this case the β phase has a wide range of solid solubility at high temperatures, but at low temperatures the solid solution is of limited extent, the limits, according to the most recent determinations, being from about 53.5 to 50.0% copper according to the microscopic work of Gayler, and the conductivity work of Haughton and Griffiths, but from 54.5 to 49% copper according to Soldau. The equi-atomic alloy (CuZn) here contains 49.3% Cu, but the minimum on the resistance curves is reached at about 50-51% copper.

These most interesting results may be summarized by saying that in the case of these intermediate phases of variable composition, the conductivity and temperature-coefficient curves rise to maxima at or near to some simple atomic ratio, but at present it does not seem justifiable to say more than this. In the preceding chapter we described in detail the interesting phenomena met with if copper-gold alloys were submitted to prolonged annealings, when the atoms, which were at first arranged at random

on a common lattice, gradually rearranged themselves in a definite pattern, and it is extremely probable that the same kind of change may take place in secondary solid solutions, in which case conductivity measurements, unchecked by X-ray crystal analysis, may easily lead to wrong conclusions, for the alloy may appear quite homogeneous under the microscope before the complete atomic rearrangement has taken place. The crystal structures of some of these intermediate phases have in fact been determined—thus the β phases of the copper-zinc and gold-zinc alloys possess the body-centred cubic type of structure, and the equi-atomic alloy on prolonged annealing has the caesium chloride type of structure, with one kind of atom in the centre of the unit cube, and the other kind of atom at the corners. But in general these determinations have been carried out independently of the electrical work, so that the exact state of the specimens used for the conductivity measurements is unknown. It is in fact quite possible that phases such as the α_1 and α_2 phases of the gold-zinc alloys which we have just described are formed by processes similar to those which take place on the prolonged annealing of the copper-gold alloys dealt with in the previous chapter, but whether these are to be looked upon as definite compounds or as symmetrical solid solutions is a question which the conductivity measurements alone cannot answer.

It seems, however, to be established quite definitely that, using specimens annealed for a time sufficient to make them homogeneous when examined under the microscope, the maxima on the conductivity curves do not always occur exactly at a simple atomic ratio. But Soldau's conclusion that in such cases the phase consists of a solid solution in a partly decomposed compound, does not appear to be established. For, in some cases at any rate, the maxima on the conductivity and temperature-coefficient curves do not occur at the same composition, whilst the conclusion that the position of the maximum approached the simple atomic ratio as the temperature was lowered, was in reality based on drawing smooth curves in a very arbitrary way through a comparatively small number of points.

In contrast to the secondary solid solutions just described, there are others in which the conductivity diminishes as we proceed from some simple atomic ratio. An example of this kind is the so-called ' γ ' solid solution in copper-zinc alloys (' γ ' brass), the composition of which extends from about 62 to 70 per cent. of zinc. The X-ray investigation of Bradley and Thewlis shows that

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this solid solution is formed by substituting zinc atoms in the compound Cu_5Zn_8 ($= 62\% \text{ Zn}$), so that there is practically no solubility on the copper side of the compound. In this case the work of Puschin and Rjaschsky shows that the conductivity increases continuously as we pass from the copper-rich to the zinc-rich side of the solid solution. As we shall see later (p. 335), such phases are probably co-valent structures in which the fundamental formula, in this case Cu_5Zn_8 , gives just the number of valency electrons required to form the co-valent bonds, so that on substituting divalent zinc atoms for univalent copper atoms, free electrons are introduced with an increase in conductivity. At a sufficiently low temperature it is probable that this distinction between the two classes of solid solutions will be general, unless the formation of the solid solution involves a very great distortion of the lattice of the parent compound, but experimental data are at present lacking.

Very little systematic work has been carried out on the effect of conditions other than temperature upon the resistance of inter-metallic compounds and secondary solid solutions. It has been shown by Ufford⁵ that alloys of compositions near to those of the compounds Li_3Sn_2 , PbCa_2 , and PbCa have pressure coefficients intermediate between those of their component elements, but otherwise there is little knowledge of the effect of pressure, and some of the experimental results are of practically no value, owing to the fact that the alloys were not annealed to equilibrium.

Kapitza investigated the effect of a transverse magnetic field upon the resistance of the compound Cu_3As , and found that, unlike a solid solution, it underwent a definite increase in resistance, and behaved like a pure metal.

The problem of the factors affecting the conductivities of the intermediate phases of alloys is thus far from being solved, and much interesting work remains to be done, but it is essential that in future work in this connexion, great attention shall be given to the metallurgical treatment of the specimens, and that X-ray crystal analysis shall be used whenever solid solutions are subjected to prolonged annealing.

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IV

THE THERMAL CONDUCTIVITY OF PURE METALS

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1. General

ONE of the great characteristics of metals is that they are, in general, very good conductors of heat, and at ordinary temperatures are much better conductors than non-metallic substances. This characteristic is closely connected with the ultimate structure of metals, and the thermal conductivity is thus of great theoretical interest. But apart from this, the high thermal conductivity is of practical importance in the everyday uses of metals and alloys, and many of the more recent developments in high-speed machinery, internal-combustion engines, &c., are really only possible because the thermal conductivity of metals is great enough to enable the heat generated in the machine to be withdrawn sufficiently rapidly.

In spite of this double importance, however, our knowledge of thermal conductivity and the factors which affect it is very much less than our corresponding knowledge of electrical conductivity. This is largely owing to the fact that the electrical measurements are very much more easy to carry out than the corresponding thermal measurements. For in the case of electrical conduction, using ordinary voltages and current-densities, a metal is almost completely insulated by the usual surrounding media, such as air, oil, &c., and the whole of the electricity passing through the conductor can be controlled and measured. On the other hand, in the case of thermal conduction, heat is continually being transferred to or from the surrounding medium, so that any absolute determination of the flow of heat in the metal is made more difficult, whilst even a comparative measurement is subject to considerable error.

For convenience we deal with the *specific thermal conductivity*, K , which is defined as the amount of heat which passes across unit area in unit time under unit temperature gradient, or

more generally if heat is flowing down a bar of metal, then at any point

$$dQ$$

where K = specific thermal conductivity;

A = cross-sectional area of the bar;

$-\frac{d\theta}{dx}$ = temperature gradient along the bar at the point considered;

dQ = amount of heat which flows through the bar at this point in time dt .

The accurate methods for the determination of K will not be considered in detail here, but will be found in the papers given in the list of references. These methods involve many details and minor corrections, and great care is needed in comparing numerical values obtained by different methods.

The values of K can be expressed in different units which may at first cause some confusion. Referring the above equation to unit-temperature gradient, it will be seen that $K = \frac{dQ}{A dt}$. If the heat be measured in calories, then K is expressed in calories/cm.² sec. Since, however, many of the experimental methods involve electrical methods, the heat energy may also be expressed in watts, in which case K is expressed in watts/cm.², the two units being connected by the relation

$$\text{Unit of } K = 1 \text{ watt/cm.}^2 = 0.2389 \text{ cal./cm.}^2 \text{ sec.} = 10^7 \text{ ergs/cm.}^2 \text{ sec.}$$

In order to give a general idea of the magnitudes involved, Table XXI has been included, and from this it will be seen that, at ordinary temperatures, the specific thermal conductivities are of the order 0.1 to 1 cal./cm.² sec., but that some of the border-line metals such as antimony and bismuth show lower values.

The accuracy of the experimental methods does not at present enable us to decide whether the thermal conductivity is really independent of the temperature gradient, as is usually assumed. In the case of the electrical conductivity, the specific conductivity, in agreement with Ohm's Law, is independent of the applied electromotive force, but whether the same relation holds between thermal conductivity and temperature gradient cannot be regarded as established to any high degree of accuracy.

TABLE XXI. *The Thermal Conductivities (K), and the Wiedemann-Franz Ratios (Z) for pure metals. Unless otherwise stated the figures refer to 0°C.*

<i>Name of Metal.</i>	<i>Thermal Conductivity K in cal./cm. sec. °C.</i>	<i>Wiedemann-Franz Ratio of Thermal to Electrical Conductivity × 10⁸.</i>
Lithium . .	0.155	134
Sodium . .	0.32	138
Magnesium . .	0.37	153
Aluminium . .	0.485	136
Potassium . .	0.238	155
Iron . . .	0.147	194
Cobalt . . .	0.165 (impure)	149
Nickel . . .	0.14	169
Copper . . .	0.926	150
Zinc . . .	0.27	160
Molybdenum . .	0.35	201
Rhodium . . .	0.214	101
Palladium . . .	0.161	142
Silver . . .	1.0	152
Cadmium . . .	0.228	157
Tin . . .	0.157	163
Antimony . . .	0.044	145
Tantalum . . .	0.13	188
Tungsten . . .	0.382	195
Iridium . . .	0.14	116
Platinum . . .	0.167	161
Gold . . .	0.71	160
Mercury . . .	0.066 (−44°)	—
Thallium . . .	0.093	157
Lead . . .	0.083	165
Bismuth . . .	0.02	214

2. Thermal Conductivities and Wiedemann-Franz Ratios for Single Crystals and Polycrystalline Metals

When Table XXI is compared with the previous Table II for the electrical conductivities, it will at once be seen that those metals which are good conductors of electricity are also good conductors of heat. This is in fact one of the great characteristics of pure metals, and is summarized in the well-known *Wiedemann-Franz Law*, which states that at ordinary temperatures the ratio of the thermal and electrical conductivities is approximately constant for all metals, and, at 0° C., equals about 140×10^{-8} where

K is expressed in calories.* The constancy of this ratio, which is known as the Wiedemann-Franz ratio, is shown in the third column of Table XXI, and we shall denote the ratio by the symbol $Z = \frac{K}{C}$, but it will be seen that the constancy of the ratio is far from exact.

The above data all refer to metals in the normal polycrystalline condition, but, as with the electrical conductivity, the results are slightly different in the case of single crystals. Our knowledge of these phenomena is at present very scanty, but Bridgman¹ has investigated the thermal conductivity of the non-cubic metals zinc, bismuth, cadmium, and tin, and the results obtained are of great interest. The crystals of these metals have rotational symmetry, and the thermal conductivity, like the electrical conductivity, can be expressed in terms of two constants, namely, the conductivities parallel and perpendicular to the axis of symmetry. We may denote these conductivities by the symbols K_{\parallel} and K_{\perp} , and for convenience may use terms γ_{\parallel} and γ_{\perp} to denote the reciprocals of the two conductivities or the thermic resistances, where

$$\gamma_{\parallel} = \frac{1}{K_{\parallel}}, \text{ and } \gamma_{\perp} = \frac{1}{K_{\perp}}.$$

The results at ordinary temperatures are then in agreement with the symmetry relations of Voigt expressed in the form

$$\gamma_{\theta} = \gamma_{\perp} + (\gamma_{\parallel} - \gamma_{\perp}) \cos^2 \theta,$$

where γ_{θ} means the thermic resistance in any direction inclined at an angle of θ with the axis of symmetry.

In the case of some of these non-cubic metals the thermal conductivity varies very greatly with the grain size. Thus, according to Bridgman,¹ the thermal conductivities of single crystals of cadmium, zinc, and tin were about 20% greater than the normal polycrystalline metal, whilst for bismuth the difference was as much as 200%. A large difference for bismuth, and also for antimony, was confirmed by Eucken,⁶ although according to Kaye and Roberts⁵ the difference for bismuth is only about 20%. Bidwell and Lewis⁷ found a difference of 18% between single crystal and polycrystalline zinc, although for cadmium a much smaller variation was reported by Eucken.⁹ It seems, however, to be quite clear that for the non-cubic metals in Groups II B and V B, the thermal conductivity is considerably affected by grain

* In absolute units the value of the Wiedemann-Franz Ratio is about 6×10^{10} E.M.U.

size at ordinary temperatures, and that this difference increases at low temperatures.

On the other hand, in the case of metals crystallizing in the cubic system the effect of grain size is very much less pronounced at ordinary temperatures. Thus E. Griffiths² found very little difference between the thermal conductivities of a single crystal of aluminium and the normal polycrystalline metal, and this was confirmed by an isolated value given by Calthrop.³ Grüneisen and Goens⁴ found that for the cubic metals gold, copper, and aluminium, the conductivity was but little affected by the grain size, and according to Kannuliik and Laby⁸ the difference between the thermal conductivity of single crystal and polycrystalline copper is only about 4%, and these general results were confirmed by Eucken and Dittrich.¹⁰ At low temperatures Grüneisen and Goens found no marked increase in the effect of grain size, in contrast to the non-cubic metals, but in the case of electrolytic iron Eucken and Dittrich¹⁰ found the difference to increase slightly. It seems, however, to be quite well established that for cubic metals the effect of grain size upon thermal conductivity is much less pronounced than in many of the non-cubic metals.

In the case of the non-cubic metals referred to above, the thermal conductivity varies with the orientation, and according to Kaye and Roberts the thermal conductivity of bismuth parallel to the trigonal axis is 0.0159, and at right angles to the trigonal axis is 0.0221. Bridgman stated that for all the above metals the thermal conductivity varied with the orientation so as to satisfy the symmetry relations of Voigt, but the exact figures were not published. It was, however, considered of great interest to see whether the Wiedemann-Franz ratio was constant in different directions in the crystals or not, and for this purpose the electrical and thermal conductivities were measured on the same set of specimens.

According to the symmetry relations described above, the thermal resistance in the direction making an angle of θ with the axis of symmetry is given by the expression

$$\gamma_{\theta} = \gamma_{\perp} + (\gamma_{\parallel} - \gamma_{\perp}) \cos^2 \theta.$$

The electrical resistance W is given by an expression of the same type, namely, $W_{\theta} = W_{\perp} + (W_{\parallel} - W_{\perp}) \cos^2 \theta$.

Eliminating θ between these expressions, we obtain

$$\gamma_{\theta} = \frac{W_{\theta}(\gamma_{\parallel} - \gamma_{\perp}) + W_{\parallel}\gamma_{\perp} - W_{\perp}\gamma_{\parallel}}{W_{\parallel} - W_{\perp}}$$

so that γ_θ , the thermal resistance in a direction θ , is a linear function of W_θ , the electrical resistance, and the graph between the two should be a straight line. If, however, the Wiedemann-Franz Law holds in every direction, then γ_θ must not merely be a linear function of W_θ , but the two must be directly proportional, and the straight line must pass through the origin.

The actual values obtained by Bridgman were subject to considerable experimental error, and in the case of tin the results were inconclusive. For bismuth the position was doubtful, but the difference was in the same direction as that given by the independent work of Kaye and Roberts. For zinc and cadmium, however, it was considered by Bridgman that there was 'no room for doubt that the experimental points do not lie within the experimental error on the line through the origin, so that for these metals the Wiedemann-Franz proportionality does not hold for different directions in the crystal'.

It may therefore be taken as conclusively established that the thermal conductivity varies with the direction in a non-cubic crystal, and as probable that the Wiedemann-Franz ratio is not the same in all directions in crystals of bismuth, zinc, and cadmium, although the experimental accuracy is here rather low.

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3. The Effect of Temperature upon Thermal Conductivity

One of the great differences between the electrical and thermal conductivities of metals is that the thermal conductivities at ordinary or high temperatures are almost independent of the temperature. This is well shown in Table XXII, in which the figures are taken from the work of Schofield.¹ The approximate constancy of the thermal conductivity is in marked contrast to the rapid decrease in electrical conductivity which takes place when the temperature is raised. The general tendency is for the thermal conductivity to decrease slightly as the temperature is raised, but there are exceptions such as aluminium, although comparison is not always justified on account of the varying degrees of purity of the samples used.

TABLE XXII

<i>Metal.</i>	<i>Temperature.</i>	<i>Thermal Conductivity K in c.g.s. units.</i>
Aluminium 99.7 % Al	130° C.	0.528
	150° C.	0.527
	253° C.	0.536
	370° C.	0.542
Copper 99.9 % Cu	95° C.	0.901
	178° C.	0.893
	266° C.	0.888
	473° C.	0.858
	625° C.	0.842
Zinc 99.8 % Zn	25° C.	0.258
	54° C.	0.246
	80° C.	0.241
	103° C.	0.238

As regards the thermal conductivity at temperatures below the normal, an extensive series of measurements was carried out by Lees² over the range -170°C. to $+30^{\circ}\text{C.}$ (i.e. 103°Abs. to 303°Abs.), and the general conclusion reached was that the thermal conductivity varied but slightly over this range of temperature, the general tendency being for the conductivity to increase as the temperature was lowered. This work was carried down to the lowest temperatures obtainable by means of liquid air, and some typical results are shown in Table XXIII.

The Thermal Conductivity of Pure Metals

TABLE XXIII

<i>Metal.</i>	<i>Temperature.</i>	<i>Thermal Conductivity λ</i>
Copper . .	+26° C.	0.910
	-166° C.	1.105
Silver . .	+33° C.	0.961
	-163° C.	0.992
Zinc . .	+24° C.	0.262
	-174° C.	0.283
Cadmium .	+24° C.	0.216
	-177° C.	0.235
Aluminium .	+19° C.	0.500
	-166° C.	0.528
Lead . .	+23° C.	0.0828
	-164° C.	0.0926
Iron . .	+13° C.	0.146
	-160° C.	0.150
99.4 % Fe		
Nickel . .	+28° C.	0.138
	-159° C.	0.129

The work has been carried down to the still lower temperatures obtainable by means of liquid hydrogen, and results for copper have been published by Meissner,³ and for aluminium, cadmium, lead, and copper by Schott,⁴ whilst Onnes and Holst⁵ have determined the thermal conductivity of mercury at temperatures as low as 4° Abs.

Taken as a whole, these results show that the thermal conductivity is almost independent of temperature down to about 180° Abs. (i.e. -93° C.), but then begins to increase, at first slightly, and then more rapidly. The results of Meissner for copper agreed very well with those of Lees in the region in which the two series of determinations overlapped, and these values are shown in Fig. 21 in which the one curve shows $\gamma = \frac{1}{K}$, the reciprocal of the thermal conductivity, plotted against the absolute temperature, and this kind of relation may be taken as typical. In the case of mercury the thermal conductivity has been measured by Onnes and Holst at temperatures as low as 3.7° Abs. The mean value of K between 4.5° and 5.1° was 0.27, and between 3.7° and 3.9° was 0.40, so that the thermal conductivity increases comparatively rapidly at these low temperatures, and it seems likely that in the case of pure metals it will become infinite at the absolute zero.

It is, however, particularly to be noted that there is no discontinuity in the thermal conductivity at the temperature at which the electrical supra-conductivity appears.

We have already shown that at ordinary temperatures the ratio of the thermal conductivity to the electrical conductivity is approximately constant for all metals in accordance with the well-known Wiedemann-Franz Law. Since the thermal conductivity is practically independent of temperature above 180° Abs.,

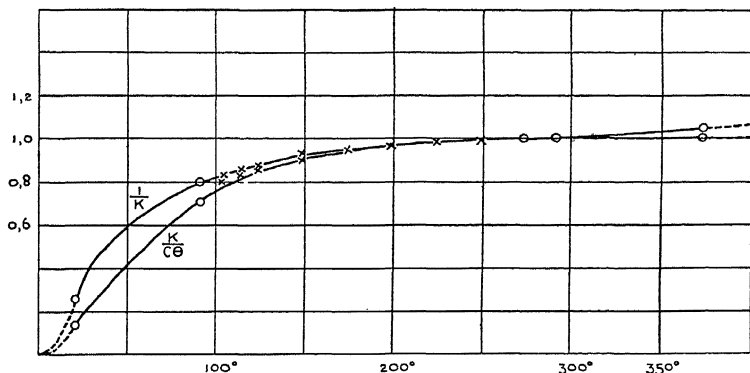


FIG. 21. Curves showing the thermic resistance $\frac{1}{K}$ and the Lorentz factor $\frac{K}{C\theta}$ for copper at different temperatures.

whilst the electrical conductivity is roughly inversely proportional to the temperature, it follows that the Wiedemann-Franz ratio varies approximately as θ , and that the expression $\frac{K}{C\theta}$ is a constant for any one metal, and is very nearly the same for all metals. This expression $\frac{K}{C\theta}$ is known as the *Lorentz Constant*, and we shall denote this by L , where $L = \frac{K}{C\theta} = \frac{Z}{\theta}$, where Z is the Wiedemann-Franz ratio.

Table XXIV will give some idea of the variations which are found at temperatures above about -100° C.

From this it will be seen that the Lorentz constant is more nearly an exact constant for any one metal over a range of temperatures than it is from one metal to another at the same temperature. Owing to the difference in purity of the different metals it is not possible to generalize the variations of the factor

$L = K/C\theta$, for it seems to be a general rule that the variations are greater as the samples are less pure.

TABLE XXIV

Metal.	Purity.	Observer.	Value of Lorentz Function $K/C\theta \times 10^6$ (K in watts/cm. °C.; C in reciprocal ohms/cm.).								
			-100° C.	18° C.	100° C.	200° C.	300° C.	400° C.	500° C.	600° C.	700° C.
Aluminium	99.9%	Lees	1.81	2.13	---	---	---	---	---	---	
	99.7	Schofield	---	---	2.23	2.36	2.44	2.53	---	---	
Copper	---	Lees	2.17	2.32	---	---	---	---	---	---	
	99.9	Schofield	---	---	2.31	2.36	2.34	2.37	2.34	2.35	
Zinc	---	Lees	2.39	2.43	---	---	---	---	---	---	
Nickel	99.2	---	---	2.26	2.26	2.29	---	---	---	---	

At lower temperatures, however, the direct correspondence between thermal and electrical conductivity no longer holds, and the term $K/C\theta$ becomes increasingly smaller. This is shown for copper in Fig. 21, in which the second curve represents the values of the Lorentz factor—no longer a constant—at various temperatures.

As we shall see later, the question of this variation of the Wiedemann-Franz ratio at low temperatures is of great theoretical importance, and much work has been done in this connexion. Grüneisen and Goens⁶ investigated the thermal conductivities of the metals gold, platinum, copper, tungsten, rhodium, aluminium, and iron, all of which crystallize in the cubic system. The thermal conductivities of different samples were measured at temperatures down to that of liquid hydrogen, and it was found that the values were greatly affected by the purity and exact condition as regards working, internal stress, &c. When, however, the thermic resistances γ (the reciprocals of the thermal conductivities) for different samples of the same metal at a particular temperature were plotted against the specific electrical resistances at the same temperature, it was found that approximate straight lines were obtained. The slopes of these lines were almost the same for different metals at different temperatures, but the lines did not pass equally near the origin.

This fact was considered by Grüneisen and Goens to indicate that, just as the specific electrical resistance of a metal can be regarded as composed of two factors, the resistance $[W_0]$ of the pure metal, and the resistance ζ , caused by impurities, strains, &c., so the thermic resistance can be regarded as composed of a metallic and a non-metallic part, of which the metallic part varies directly as the electrical resistance, in accordance with the

Wiedemann-Franz Law, whilst the non-metallic part is regarded as approximately constant. They therefore wrote

$$\gamma = \gamma_m + \gamma_i = \frac{1}{L} \cdot \frac{W}{\theta} + \gamma_i \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where γ_m and γ_i are the metallic and non-metallic parts of the thermic resistance, and W is the specific electrical resistance.

This point of view, however, leads to many difficulties which have been discussed by Eucken,⁷ and later by Grüneisen. In the first place the comparison with electrical resistance is not really justified. In the case of electrical conductivity we deal with the flow of electrons through the metal, and it is quite reasonable to suppose that the resistance to this flow may be split up into two parts, one characteristic of the metal, and the other due to impurities. In the case of thermal conductivity, however, we deal with the transference of heat by two processes, the one similar to that taking place in non-metallic solids, and the other, in some way connected with the electrical conductivity, as is shown by the approximate constancy of the Wiedemann-Franz ratio, at a given temperature. It is therefore the *thermal conductivity*, K , and not the thermic resistance, which should be the sum of two factors. Eucken therefore adopts the policy of writing the thermal conductivity as the sum of two terms, one metallic (K_m), and the other non-metallic (K_i), so that

$$K = K_m + K_i \quad . \quad . \quad . \quad . \quad . \quad (2)$$

According to Eucken's experiments on non-metallic substances, such as salts, the thermal conductivity may be expressed in the form

$$K_i = \frac{1}{A}$$

where A corresponds to the pure substance, and the term $B\zeta$ to the effect of impurities, the factor $B\zeta$ being almost independent of temperature, although A varies with the temperature particularly as the absolute zero is approached.*

We have therefore

$$K = K_m + K_i = K_m + \frac{1}{A + B\zeta},$$

* In his original paper Eucken wrote the expression in the form $\frac{1}{A\Delta}$

but he later (see p. 78) assumes that the Δ term measures the same deformation of the lattice as that which creates the additional electrical resistance (see p. 10), and therefore now writes $B\zeta$, where B is a dimension factor, and ζ the additional electrical resistance.

and if we assume that the metallic part of the thermal conductivity obeys the Wiedemann-Franz Law we may put this in the form

$$K = \frac{L_m \theta}{[W]} + \frac{1}{A+B\zeta} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Eucken then assumed that the term ζ in his expression for the thermal conductivity of non-metallic substances corresponded to the additional electrical resistance caused by impurities, &c., in the metal. If this is so we may write $\zeta = [W] - [W_0]$ where $[W_0]$ is the specific resistance of the absolutely pure metal, and in this

case, if we write γ , γ_m , and γ_i for $\frac{1}{K}$, $\frac{1}{K_m}$, $\frac{1}{K_i}$ respectively, the expression may be written in the form

$$\gamma = \frac{A - [W_0]B}{\frac{\gamma_i}{\gamma_m} + 1} + \frac{[W]B}{\frac{\gamma_i}{\gamma_m} + 1} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

In this case, since A , $[W_0]$, and B are constants at a given temperature, the linear relation between γ and $[W]$ will only hold

if $\frac{\gamma_i}{\gamma_m}$ is constant for specimens of different purity, and this is contrary to the facts.

Eucken then investigated whether an expression such as (3) could be made to fit the experimental facts, and found that if L_m , at a given temperature, be assumed independent of the purity, deformation, &c., of the specimen, a fairly good agreement can be obtained at this one temperature, but that L_m then varies with the temperature, so that the Wiedemann-Franz-Lorentz Law breaks down not merely when applied to the total thermal conductivity, but also when confined to the metallic part of the thermal conductivity alone.

It must be admitted that the treatment of Eucken involves the assumption that the behaviour of the non-metallic part of the thermal conductivity of a metal will be the same as that of a salt, and for this reason the argument cannot be regarded as completely satisfactory, since the mechanical properties, interatomic distances, &c., are quite different in the two classes of bodies. It seems, however, to be quite certain that if the conception that the heat is carried by two processes, one resembling that of non-metallic substances, and the other peculiar to metals,

be correct, it is the conductivity and not the thermic resistance which should be the sum of two factors. The linear relation between the thermic and electrical resistances is in fact only an approximate one, and begins to break down in cases where, owing to impurities or excessive strain, &c., the non-metallic part of the thermal conductivity is no longer very small compared with the metallic part. In some cases, at any rate, almost as good a straight line is obtained if one plots the thermal conductivity against the electrical conductivity, instead of plotting the resistances, and the truth appears to be that in both cases the linear relation is only approximate, and holds merely for those specimens in which the non-metallic part of the thermal conductivity is small relative to the metallic part. It is for this reason that in the conductivity curves the departure from linearity is most obvious for those points lying near the origin, whilst in the resistance curves it is those points far from the origin which show the greatest deviation.

The question whether the metallic part of the thermal conductivity obeys the Wiedemann-Franz-Lorentz Law at low temperatures is thus not completely solved, although if the arguments of Eucken be accepted the Law must be looked upon as breaking down.

It will be noted that so far we have made no assumptions as to the mechanism by which heat is transferred. This can only be done by introducing the various electronic theories which will be considered later.

The Equations of Bidwell.

It has recently been shown by Bidwell⁸ that a comparatively simple relation exists between the thermal conductivity, specific heat, and absolute temperature. This relation may be written in the form

$$K = A$$

where K is the thermal conductivity, C_p the atomic heat, and A and B are constants. For lithium the law holds as far down as -200°C. , and for sodium, lead, and zinc the agreement holds to even lower temperatures. This expression again suggests that the thermal conductivity is the sum of two terms, but it does not seem possible to identify it with the equation of Eucken by means of the equation of Grüneisen (p. 16) connecting the electrical resistance with the atomic heat. For if $K_m = LC\theta$ as the

Wiedemann-Franz-Lorentz Law requires, and if $W = \frac{1}{C} \propto \theta C_p$ according to the Grüneisen relation, we should expect

$$K_m = \frac{L\theta}{\frac{1}{C}} = \frac{L\theta}{A\theta C_p} = \frac{\text{Constant}}{C_p}$$

for the metallic part of the conductivity, so that the significance of the relation found by Bidwell is not yet clear.

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4. The Effect of Pressure upon Thermal Conductivity

Very little information is available on the effect of pressure upon the thermal conductivity of pure metals, but work in this connexion has been carried out by Lusana¹ and by Bridgman.² The results of these two workers are not in agreement. According to Lusana, the thermal conductivity of the eight metals investigated increased under pressure in much the same way as the electrical conductivity, so that the Wiedemann-Franz ratio remained constant, whilst according to Bridgman the effect of pressure upon thermal conductivity was sometimes positive and sometimes negative, and only in the case of zinc did the different investigations agree as to the sign of the effect. These two workers are not in agreement as to the relative accuracy of their respective methods, but on the whole it would seem that the work of Bridgman was carried out with greater accuracy and more attention to detail than that of Lusana; in particular, the work of Lusana involved a much larger correction for the effect of pressure upon the transmitting medium, the magnitude of this correction being as much as 30% per 1,000 kg., whereas the changes in thermal conductivity are at the most 3%, so that the effect of pressure on the transmitting medium must be known very accurately if the method is to be justified. It seems there-

fore probable that the results of Bridgman are to be relied upon as regards the sign of the effect, although, as pointed out by Bridgman himself, the accuracy of the method does not enable the pressure coefficient to be given to more than two significant figures. In general the work of Bridgman has been accepted in preference to that of Lusana, and we adopt this policy here since in a later note Lusana, whilst still preferring his results to those of Bridgman, admits that they are not really inconsistent with a variation of the Wiedemann-Franz ratio of the order found by Bridgman. It must, however, be admitted that an independent series of determinations by some other method would make the position much more satisfactory.

The results obtained by Bridgman are summarized in Table XXV, in which the mean values (from 0 to 12,000 kg./cm.²) of the pressure coefficients of the thermal conductivities and of the Wiedemann-Franz ratios are included. From this it can be seen that the thermal conductivity may either decrease or increase under pressure. There is no correspondence between the effect of pressure upon electrical conductivity and upon thermal conductivity; thus the electrical conductivities of copper and silver increase under pressure in the normal way, but their thermal conductivities diminish, whilst with tin and lead both conductivities increase. It can at once be seen that the Wiedemann-Franz ratio is not constant under pressure, a fact of great theoretical interest since the difference is greater than can be ascribed to the non-metallic part of the thermal conductivity.

TABLE XXV

<i>Metal.</i>	<i>Pressure Coefficient of Thermal Conductivity.</i>	<i>Pressure Coefficient of Wiedemann-Franz Ratio.</i>
Lead . .	+17.3 × 10 ⁻⁶	+6.0 × 10 ⁻⁶
Tin . .	+7.5 "	+3.0 "
Cadmium .	+7.4 "	-1.7 "
Zinc . .	+2.1 "	-2.5 "
Iron . .	+3.0 "	-2.6 "
Copper . .	-7.5 "	-9.3 "
Silver . .	-3.7 "	-7.0 "
Nickel . .	-12.0 "	-13.0 "
Platinum .	-1.6 "	—
Antimony .	-21.0 "	-10.0 "
Bismuth .	-31.0 "	-10.0 "

In the case of lead and tin, the thermal conductivity-pressure curves were not exactly linear, but flattened off, so that later

additions of pressure had relatively less effect. This deviation from linearity was comparatively slight, and was within the limits of error of the method in the case of the other metals.

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5. The Effect of Deformation upon Thermal Conductivity

The thermal conductivity, like the electrical conductivity, is affected by tension or other forces causing deformation, and we have again to distinguish between forces acting within the elastic limit of the material, and forces which produce permanent deformation. Unfortunately the existing data are very scanty, and are not always in good agreement.

The early work of A. Johnstone¹ and of N. F. Smith² indicated that thermal conductivity is increased by tension, but this was not confirmed by the later and more accurate work of Bridgman,*³ who measured the effect of tension upon the thermal and electrical conductivities of the same set of specimens. According to these results, both the thermal and electrical conductivities are diminished by tension in all the metals examined except nickel, which shows the opposite effect. The two conductivities are, however, not affected to the same degree by the application of tension, so that the Wiedemann-Franz ratio is not constant. In this work it was considered that the forces applied were within the elastic limit in all cases except for aluminium, with which permanent deformation occurred.

Some typical results are shown in Table XXVI, from which it can be seen that sometimes the thermal conductivity is affected more than the electrical conductivity, whilst sometimes the reverse is the case. The probability that Bridgman's work is correct as regards the general effect of tension on thermal conductivity is strengthened by the fact that Lees and Calthrop⁴ found that the thermal conductivity is slightly decreased by torsion. These workers investigated the effect of torsion on both electrical and thermal conductivities of copper, aluminium, and lead, and found that the relative effect of torsion on thermal conductivity was greater than that on electrical conductivity. The decrease in thermal conductivity was of the order of a few tenths

* For a discussion of the relative accuracy of the methods see Bridgman, *Proc. Amer. Acad.* 1923, 59, 119.

TABLE XXVI

Metal.	Proportional Change of Specific Conductivity per kg./cm. ²		Load in kg./cm. ²
	Thermal $\times 10^6$.	Electrical $\times 10^6$.	
Aluminium .	—3.8	—1.8	*
Copper . .	—2.1	—1.7	1080
Iron . . .	—1.90	—1.82	2050
	—2.37	—1.80	1025
Palladium .	—0.20	—1.52	770
Nickel . .	+0.48	+3.3	1900

per cent., and was roughly proportional to the square of the twist for the small twists employed; these were from 0 to 1.84° twist per centimetre length of the test wire. These results are in agreement with those of Smith, but are not quite conclusive as to the effect in normal metals since the specimens were not annealed. They do, however, show that the Wiedemann-Franz ratio is not a constant under torsion.

Measurements on single crystals of aluminium under torsion have been made by Calthrop,⁵ but were inconclusive, the effect of torsion being sometimes positive and sometimes negative, and always very small and indistinguishable from that of pure annealed polycrystalline metal. In view of the fact that the very accurate work of Hanson and Gough showed that the single crystals of aluminium had no detectable primitive elasticity, it seems probable that the elastic limit was exceeded in the torsion experiments, and that the observed results were a combination of plastic deformation on the one hand, and of true elastic torsion on the other.

As regards the effect of plastic deformation (cold-rolling, wire-drawing, &c.) the varying purity of the samples used by different workers, and also the comparative inaccuracy of thermal conductivity measurements, make it difficult to generalize, and the data are in some cases contradictory. According to Grüneisen and Goens⁶ the thermal conductivities of gold, platinum, copper, tungsten, and aluminium at —190° C. are always greater for annealed material than for specimens of the same metals after hammering, drawing, or other permanent deformation. Thus a sample of technically pure gold, hammered and unannealed, had a thermal conductivity of 2.90 at —190° C., and after annealing for three hours at 390° C. the thermal conductivity (at —190° C.)

* Mean value at loads of 545 and 393 Kg./cm.²

rose to 2.93. The corresponding values at -252° C. were 3.53 and 4.17, so that the effect is relatively greater as the temperature is lowered.

On the other hand, at ordinary temperatures the work of some investigators appears to indicate that permanent deformation increases the thermal conductivity of metals, and it has sometimes been concluded that this is the general rule. Thus Calthrop found that the thermal conductivity of hard-drawn aluminium wire of 99.6% purity was 0.495, whilst the conductivity of the same sample of wire in the annealed state was 0.490. The position is thus inconclusive, and it is possible that deformation may increase the thermal conductivity at normal or high temperatures, and diminish it at low temperatures, although with some metals such as aluminium it is more probable that the conflicting results are due to the fact that the annealing process may send impurities into solid solution. Thus most specimens of unannealed aluminium, even of 99.8% purity, contain small particles of silicon, and of a compound FeAl_3 which can be detected microscopically. On prolonged annealing, the silicon may pass into solid solution with a slight decrease in electrical, and hence presumably also in thermal conductivity. This effect was noticed in the work of Fraser described on p. 6.

It will be noticed that all these experiments on the effect of pressure, tension, &c., upon the Wiedemann-Franz ratio have dealt only with the ratio as determined from the total thermal conductivity, and there is thus much scope for further detailed work in which both the metallic and non-metallic parts of the thermal conductivity are considered.

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THE THERMAL CONDUCTIVITY OF ALLOYS

1. Primary Solid Solutions	85
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1. Primary Solid Solutions

AS in the case of the electrical conductivity, it is convenient to divide the intermediate phases met with in alloy systems into the three classes—primary metallic solid solutions, secondary solid solutions, and intermetallic compounds. But as the available data for thermal conductivity are so very scanty, we may consider all three types in one chapter, although dealing with each in turn. Very great care is necessary in dealing with the experimental results because of the varying purity of the metals used, and the comparatively inaccurate nature of the thermal conductivity measurements. In general it may be said that it is inadvisable to compare to more than one or two figures the absolute values obtained by different workers unless there is very definite evidence that their experimental methods would give the same results on identical specimens. On the other hand the general nature of the results obtained by one worker may be compared with those of another to a much higher degree of accuracy, since here any error due to one method will be the same throughout.

In the case of *primary solid solutions*, the general form of the thermal conductivity-composition curve is the same as that of electrical conductivity. That is to say, the thermal conductivity of a metal is greatly lowered by the presence of a second metal in solid solution, and if the two metals be completely miscible so that a continuous series of solid solutions is formed, the conductivity-composition curve has the typical U-shaped form. Examples of this type are the gold-silver, copper-nickel, palladium-gold, palladium-silver, and palladium-copper alloys which have been investigated by Sedstrom* in 1924,¹ whilst earlier work on these and other alloys was carried out by Schulze in 1911.²

* It should be noted that Sedstrom's figures for thermal conductivity were not obtained by direct measurement but were calculated from thermoelectric measurements by a method due to Borelius (*Ann. d. Physik.* 1917, 52, 398). In the case of palladium-gold and palladium-silver alloys the figures obtained by Sedstrom and direct measurements by Schulze agree as to the type of variation but differ in absolute value by as much as 30% in some cases. Borelius considered the method satisfactorily established.

As typical of these we may describe the results for copper-nickel alloys shown in Fig. 22 and Table XXVII, in which the values for the thermal conductivity and Wiedemann-Franz ratio are given.

TABLE XXVII
*Thermal Conductivity and Wiedemann-Franz Ratio
of Copper-Nickel Alloys (Sedstrom).*

<i>Atomic % Ni.</i>	<i>Electrical Conductivity $C \times 10^{-6}$ at 0°.</i>	<i>Thermal Conductivity Watts K in cm^2 at 0°.</i>	$Z = \frac{K}{C}$
0.0	0.526	3.55	68
2.3	0.213	1.53	72
4.6	0.130	0.94	72
8.8	0.0806	0.62	77
9.8	0.0735	0.59	80
18.4	0.0410	0.39	95
30.1	0.0278	0.26	94
38.1	0.0235	0.22	93
43.0	0.0219	0.21	96
50.1	0.0202	0.20	99
55.6	0.0192	0.20	104
58.5	0.0190	0.19	100
62.0	0.0193	0.19	99
69.6	0.0203	0.21	103
75.3	0.0240	0.21	88
78.6	0.0273	0.25	92
88.8	0.0431	0.33	77
94.8	0.0553	0.39	71
100.0	0.0901	0.59	66

These results may be taken as typical of those found by Sedstrom and by Schulze for non-ferrous alloys forming a complete series of solid solutions, and they lead quite definitely to the conclusion that, although both conductivities when plotted against the composition of the alloys show the same general U type of curve, the two conductivities are not lowered proportionally, so that the Wiedemann-Franz ratio is not a constant, but rises to a maximum value.

In the case of primary solid solutions of limited extent, the German workers have been led to the same general conclusion—that is to say, the thermal conductivity diminishes rapidly when one metal dissolves in another in the solid state. As long as the solid-solubility limits are not exceeded, the curve connecting

the composition of the alloy and its thermal conductivity is of the same general type as that met with in the case of alloys forming a continuous solid solution. If the solid solution has only a narrow range of composition the thermal conductivity curves fall sharply as shown in the left-hand diagram of Fig. 23, whilst if the solid solution extends farther, the characteristic flattening is shown as in the right-hand part of Fig. 23. These

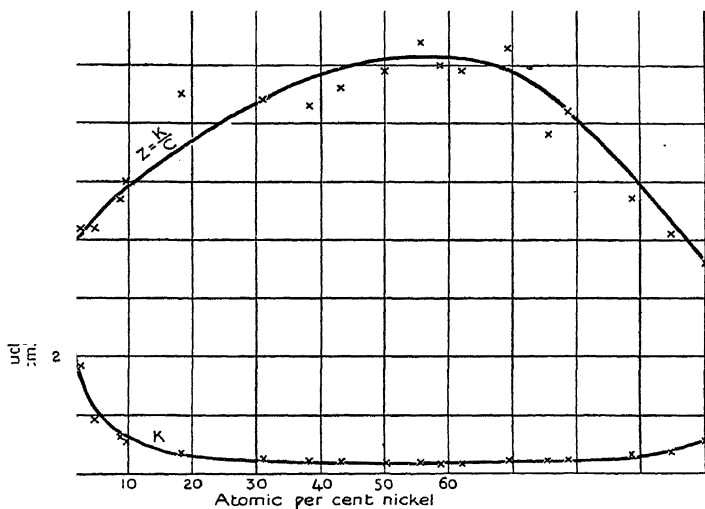


FIG. 22. Graphs showing the thermal conductivity K , and the Wiedemann-Franz ratio $Z = \frac{K}{C}$ for copper-nickel alloys.

curves may in fact be regarded simply as the end sections of the typical U-shaped curve found for cases of complete miscibility. As soon as the limit of solid solubility is reached, the alloys become heterogeneous and behave as a mixture of two phases, but as we are dealing here with single phases only, we shall not follow the complex alloys into their polyphase regions.

While, however, the results of different workers are in agreement as to the general form of these curves, there is an apparent contradiction between the results for the Wiedemann-Franz ratio. According to the German workers, the Wiedemann-Franz ratio, in the case of primary solid solutions of limited extent, increases in much the same way as in the cases of complete miscibility which we have described above. Numerous examples of this type are given by A. Schulze in the volume of Guertler's

Metallographic dealing with the thermal conductivities of alloys, and although there are occasional exceptions, the work leads unmistakably to the conclusion that the typical primary solid solution shows a Wiedemann-Franz ratio increasing with the percentage of the solute metal. In a few cases the increase is probably within the obvious experimental error of the methods, but usually this is not so, and the increase in the Wiedemann-Franz ratio is described as the general rule.

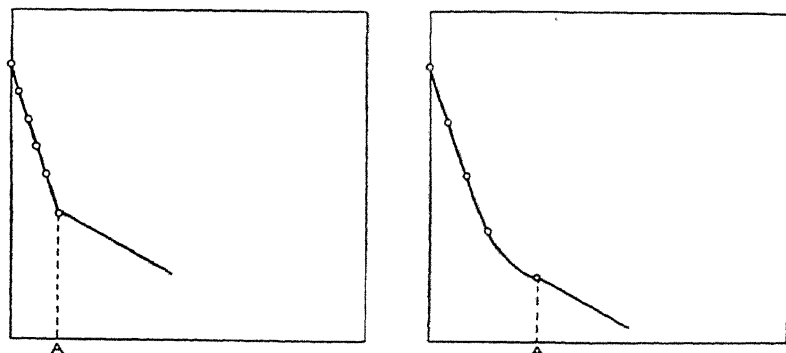


FIG. 23. Showing the types of composition-conductivity curves found for primary solid solutions of limited extent. In each case the composition *A* marks the limit of solid solubility.

On the other hand, in a recent paper by E. Griffiths³ values are given for the thermal and electrical conductivities of some non-ferrous alloys, and the conclusion is reached that the Wiedemann-Franz ratio is constant within the limits of accuracy of the methods used. The majority of the alloys examined were poly-phase, but among the results quoted were some for primary solid solutions of zinc and tin in copper (brasses and bronzes), and for various ternary alloys of copper. From the values determined it was concluded that for the six bronze alloys investigated (some of which were two-phase alloys) the Lorentz constant $\left(\frac{K}{C\theta}\right)$ was constant to within $\pm 2.5\%$ over the range 75° to 250° C., the variation being probably within the experimental error. These results were in agreement with one isolated determination by Lees in 1907, in which the Lorentz constant was determined as approximately 5.75×10^9 for pure metals, and 5.83×10^9 for a 60:40 brass, and also with a determination of Grossman's⁴ for a 10% tin, 90% copper alloy.

It is unfortunately not possible to make a direct comparison between the values found by Griffiths, and those obtained by the German workers, since the alloys investigated were not the same, but the two series of experiments seem at first sight to be contradictory, for some of the alloys investigated by Griffiths contained solid solutions, and it would be a very remarkable coincidence if the different factors cancelled out so as to give

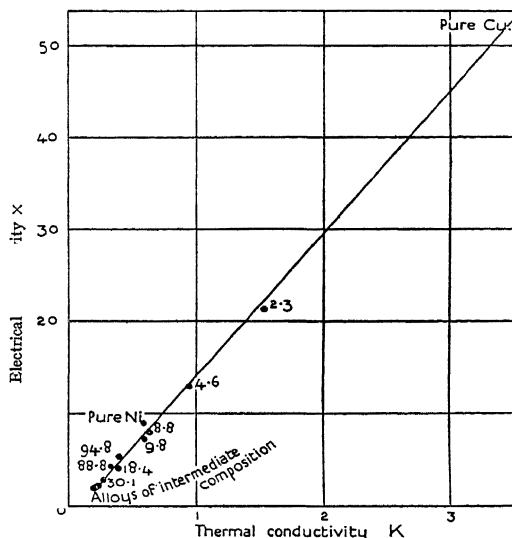


FIG. 24. The figures by each point give the atomic % nickel of the alloy concerned.

a constant Wiedemann-Franz ratio, if the ratio for a simple solid solution were a variable.

It is possible, however, that some of the apparent contradiction may be due to a phenomenon similar to that found by Eucken, and by Grüneisen and Goens. If the thermal conductivity be composed of two factors, one of which obeys the Wiedemann-Franz-Lorentz Law, whilst the other is relatively small and varies comparatively slightly, the maxima on the curves connecting the compositions and the Wiedemann-Franz ratios (calculated from the total thermal conductivities) will be accounted for, as may be shown in the following way.

Let the total thermal conductivity K be composed of a metallic part K_m obeying the Wiedemann-Franz Law, and a non-metallic part K_i .

Then the apparent Wiedemann-Franz ratio based on measurements of the total thermal conductivity will be $\frac{K}{C}$, and may be written

$$\frac{K}{C} = \frac{K_m}{C} + \frac{K_i}{C} = Z + \frac{K_i}{C},$$

where Z is the true Wiedemann-Franz ratio for the metallic part of the conductivity.

Hence $\frac{K}{C}$ will be a maximum when $\frac{K_i}{C}$ is greatest, i.e. when C is least, as in the alloys of intermediate composition. As long as K_i does not vary much with composition an approximately straight line should be obtained if the thermal and electrical conductivities be plotted against one another, and, as can be seen from Fig. 24, this is approximately the case for the copper-nickel alloys at ordinary temperatures. In this case, if the straight line be extra-polated it cuts the K axis at about 0.06, which is about 1.7% of the total thermal conductivity of copper, so that the non-metallic part of the thermal conductivity is comparatively small.

To a higher degree of accuracy the points do not all lie on one straight line, the copper-rich and nickel-rich alloys forming two curves of slightly different slopes which coincide for the alloys of intermediate composition. This indicates that the non-metallic part of the thermal conductivity is not exactly constant, and this is only to be expected since the work of Eucken (p. 77) showed that the thermal conductivities of pure salts were lowered by the formation of solid solutions. This effect may be expected to become much more important at low temperatures, and a series of measurements here would be of great interest. But at ordinary temperatures the results of the German workers are in general agreement with the conception of a thermal conductivity composed of two parts, one obeying the Wiedemann-Franz-Lorentz Law, the other part being comparatively small and approximately constant.

The non-metallic part of the conductivity is thus comparatively unimportant in alloys which have a high thermal conductivity, but in poor conducting alloys—such as the intermediate copper-nickel alloys described above—the non-metallic part of the thermal conductivity is relatively much greater, so that the Wiedemann-Franz ratio rises considerably. It is probably this which accounts for the apparent discrepancy between the results

of Griffiths, and those of the German workers. For the alloys examined by Griffiths were all comparatively good conductors, for which the non-metallic part of the conductivity was relatively unimportant, and the Wiedemann-Franz ratio was thus little affected. It must be admitted, however, that some redeterminations of the thermal conductivities of complete series of solid solutions would make the position very much more satisfactory, but the investigation should extend over a range of temperatures.

As in the case of the electrical conductivity, it seems probable that prolonged annealing may cause a change in the thermal conductivity of some primary solid solutions, either owing to the formation of definite intermetallic compounds, or to an atomic rearrangement giving rise to what we have defined as a symmetrical solid solution. Thus in the case of the copper-gold alloys which are described in connexion with the electrical conductivity, it has been found by Sedstrom⁵ that annealed alloys show a maximum thermal conductivity at the equi-atomic composition. But no maxima, either for electrical or thermal conductivities, were observed at 25 atomic per cent. gold, suggesting that the annealing was insufficient to cause the full changes found by Johansson and Linde in their work on electrical conductivity.

2. Secondary Solid Solutions and Intermetallic Compounds

In the case of secondary solid solutions and intermetallic compounds the available data are so scanty that any generalization is difficult. As for the electrical conductivity, it seems to be a general rule that the thermal conductivity of a definite intermetallic compound is always less than that of the better conducting of its two component elements, and is usually less than that of either element. On the other hand the Wiedemann-Franz ratios of intermetallic compounds appear quite indefinite, which is readily understood if the thermal conductivity is really composed of a metallic and a non-metallic part. Thus in the system antimony-cadmium, according to Eucken and Gehloff,⁶ the Wiedemann-Franz ratio for the compound SbCd is as large as 660×10^{-6} , whilst the ratios for the component elements are 7.9×10^{-6} for cadmium and 6.2×10^{-6} for antimony. But this is exceptional, and in some cases the differences between the ratio for the compound, and those for its constituent elements are within the limits of error. It seems probable, however, that it is a general rule that the Wiedemann-Franz ratio is higher, the

lower the electrical conductivity of the compound. This of course is at once understood, for the non-metallic part of the thermal conductivity becomes relatively more important as the metallic part, and hence also the electrical conductivity, becomes smaller.

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VI

THERMO-ELECTRIC PROPERTIES OF METALS AND ALLOYS

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1. General

THE term 'thermo-electric properties' is used to cover a number of phenomena, and in its broadest sense it may be said to include any thermal effect produced when an electric current is passed through a metal or across the junction between two metals, and, conversely, any electrical effect caused by the passage of a current of heat. The first and most characteristic effect is thus the *Joule Heating Effect*, which is produced when a current is passed through a conductor, and, as is well known, the amount of heat produced in this case in unit time is equal to $C^2\omega$, where C is the current strength, and ω the actual resistance of the conductor. The remaining effects are best understood by considering the case of a

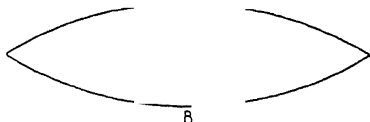


FIG. 25.

simple thermo-electric circuit, consisting of two wires of different metals A and B , with junctions at two different temperatures θ_1 and θ_2 . In the general case, if two metals are joined in this way, an electromotive force is produced, and a current flows through the circuit. We shall denote the thermo-electromotive force of such a circuit by the symbol E . With two given metals at different temperatures, E is an additive quantity, so that the thermo-electromotive force with the junctions at θ_1 and θ_n , is the algebraic sum of the thermo-electromotive forces between θ_1 and θ_2 , θ_2 and θ_3 , ... θ_{n-1} and θ_n . In practice therefore we usually keep one junction at a constant temperature, generally 0°C. , and measure the thermo-electromotive forces when the

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temperature of the other junction is varied. In this way we obtain the variation of E with θ , and the value of $\frac{dE}{d\theta}$, which is known as the *thermo-electric power*, can be determined either by drawing tangents to the curves connecting E and θ , or by expressing the relation between E and θ by semi-empirical equations which can be differentiated. In some cases the curves connecting E and θ for a particular pair of metals rise to a maximum at a certain temperature, which is called the *inversion point*, and at this temperature $\frac{dE}{d\theta} = 0$, and the thermo-electric power, which we shall denote by the symbol P , changes its sign.

The thermo-electric power $P = \frac{dE}{d\theta}$ represents the rate at which the thermo-electromotive force varies with the temperature, and is thus a measure of the sensitivity of a thermo-couple composed of the two metals concerned. If the thermo-electric powers of a metal A against two metals B and C be known, the thermo-electric power of B against C is equal to the algebraic difference of that between A and B , and A and C . Thus the thermo-electric power of copper against lead is $+3.1$ microvolts/ $^{\circ}\text{C}$., and of copper against platinum is $+7.5$ microvolts, so that the value for platinum against lead is -4.4 microvolts/ $^{\circ}\text{C}$., since the two values against copper show that the platinum is less positive than the lead.

In order to facilitate comparison the values are therefore generally reduced to a standard metal, and the most common metals used for this purpose are copper, platinum, and lead. By convention the sign is taken as positive if the current flows from the given metal A to the standard metal at the cold junction.

The thermo-electric force of a circuit is not affected by the introduction of a third metal, provided that the junctions of this metal with the other two metals are at the same temperature. Thus in Fig. 26*a* the thermo-electric force of the simple circuit of two metals represented ——— and ——— with junctions at θ_1 and θ_2 , is the same as that of the more complex circuit of three metals shown in Fig. 26*b*, provided that the points of contact A and B are at the same temperature. It is for this reason that thermo-couples can be connected to the terminals of galvanometers without introducing additional electromotive forces, although for really accurate work the two junctions may have to be in a thermostat in order to ensure that they are at the same temperature. From this point of view, the advantage of

'Manganin' over 'Constantan' for the construction of resistance boxes, &c., is that the former has a much lower thermo-electric power against copper than the latter.

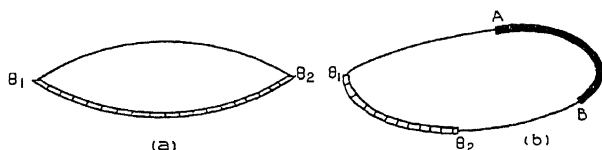


FIG. 26.

2. The Seebeck, Peltier, and Thomson Effects

In the above description we have simply accepted the fact that an electromotive force is produced in a circuit of two metals in which the junctions are at different temperatures, but actually the process is complex, and several phenomena are superimposed. At present it is universally recognized that two distinct phenomena take place in a thermo-electric circuit, and it is claimed by some workers that two additional processes are also concerned, although this is disputed by others. We shall therefore adopt the policy of describing first the effects about which there is general agreement, and later those which are uncertain.

The Seebeck and Peltier Effects.

The discovery that an electromotive force is produced in a circuit of two metals with the junctions at different temperatures was made by Seebeck in 1822, and in 1834 it was shown by Peltier that when an electric current is passed across the junction between two metals, heat is absorbed when the current is passed in one direction, and evolved when the current flows in the opposite direction. This reversal of the heat change with the direction of the current enables the so-called *Peltier Effect* to be distinguished from the ordinary Joule Heating Effect. The heat evolved or absorbed by the Peltier Effect varies directly with the current strength, and the *Peltier Constant* Π is defined by the equation

$$Q =$$

where Q is the heat evolved or absorbed by the passage of a current I for a time t .

Expressed in milli-calories/coulombs, the value of Π is usually of the order 0.1 to 3.0 for combinations of pure metals, but may be greater when one of the borderline metals such as antimony, bismuth, or silicon is involved, whilst when alloys containing

solid solutions or intermetallic compounds are used the values may be still higher.

The Peltier Constant varies greatly with the temperature, and except at very low temperatures Π generally increases with rise of temperature (see p. 99).

The Thomson Effect.

The Seebeck and Peltier Effects refer exclusively to junctions between two metals, but in 1854 it was shown by Thomson that when a current of electricity flows down an unequally heated wire, a transference of heat takes place. In some metals, such as copper, when the current is passed from a hot to a cold part, heat is evolved just as though the electricity possessed a positive specific heat, but in other metals, such as iron, the effect is in the opposite direction, and heat is absorbed when the current passes from hot to cold. This phenomenon is known as the *Thomson Effect*, and the Thomson Coefficient σ is defined by the relation

$$Q = \sigma \frac{d\theta}{dl} It$$

where Q is the heat carried by a current I , in time t , along a wire of temperature gradient $\frac{d\theta}{dl}$. σ may be measured in micro-calories/coulomb $^{\circ}$ C., or alternatively, if the energy is expressed in electrical units, σ may be measured in micro-volts/ $^{\circ}$ C.

Confusion may, however, be caused by the sign of the coefficient. In the majority of the older tables a positive Thomson coefficient means that heat is evolved when the current flows from hot to cold, so that an electric current flowing with the heat current may be said to assist the transport of heat. Since, however, the negative electrons which carry the electricity move in the opposite direction to the current, some writers prefer to give a positive Thomson coefficient to those metals in which the passage of *electrons* from hot to cold causes heat evolution, but we shall not use this convention here unless it is expressly stated.*

For most normal metals the effect is small, and σ is of the order 0.1 to 10.0 micro-volts/ $^{\circ}$ C., but there is no obvious relation between the position of the metal in the Periodic Table and the positive or negative sign of the coefficient, except that the border-

* This convention has been adopted by the compilers of the International Critical Tables, with the result that the signs given for the Thomson coefficients are the opposite of those in the earlier Landolt's Tables, and most of the literature.

line metals such as arsenic, antimony, and bismuth all show abnormally large effects. Unlike the Peltier coefficient the Thomson coefficient at ordinary temperatures is but little affected by temperature, although at lower temperatures changes occur. For metals with positive coefficients, according to Borelius and Gunneson,¹ the Thomson coefficient tends to become smaller at low temperatures (-100°C. to -150°C.) and may sometimes change sign.

As will be seen from the description on p. 102, the thermo-electric measurements at very low temperatures indicate that the effects are complex in this region.

The coefficient σ is sometimes called the 'Specific Heat of Electricity' in the metal concerned, since it indicates the heat change involved when the current of electricity flows from one temperature to another.

Relations between the Peltier and Thomson Effects and the Thermo-Electromotive Force.

The thermo-electromotive force E , the thermo-electric power P , and the Peltier and Thomson coefficients Π and σ can be related by arguments based on the first and second laws of thermo-dynamics. For this purpose we consider a thermo-electric circuit composed of two metals A and B , with junctions at temperatures θ and $\theta + d\theta$, the corresponding Peltier coefficients being Π and $\Pi + d\Pi$, and the Thomson coefficients of the two metals σ_A and σ_B . Then since, according to the first law of thermo-dynamics, energy cannot be destroyed or created, the electrical energy generated in the circuit must be equal to the heat absorbed, so that

$$dE = d\Pi + (\sigma_A - \sigma_B)d\theta \quad . \quad . \quad . \quad (1)$$

If now we consider the circuit as a reversible engine, we have according to the second law of thermo-dynamics $\Sigma \frac{dQ}{\theta} = 0$, so that

$$\theta \quad \cdot \quad \frac{\Pi}{\theta} \quad \cdot \quad \Pi + d\Pi \quad \cdot \quad d\theta \quad . \quad . \quad (2)$$

Hence, by combining (1) and (2),

$$\overline{\frac{d\Pi}{d\theta}} \quad . \quad . \quad . \quad (3)$$

where P is the thermo-electric power, and also

$$= -\theta \frac{dP}{d\theta} \quad . \quad . \quad . \quad (4)$$

Consequently, if we can express the relation between E and θ by some empirical equation, such as $E = a + b\theta + c\theta^2$, then the first differential of this will enable us to obtain Π by means of equation (3), whilst the second differential will, by means of equation (4), enable us to obtain the difference between the Thomson coefficients for the two metals. The above line of reasoning involves the assumption that the reversible thermo-electric effects can be considered independently of the ordinary thermal conduction and Joule Heating Effect, and is therefore not entirely satisfactory,* but equations (3) and (4) have been shown to hold true within the limits of accuracy of the experimental methods, the chief work in this connexion being due to Jahn,² Battelli,³ Beck,⁴ Caswell†,⁵ and Borelius.⁶ From the above equations it will be seen that the Peltier heat becomes zero at the inversion-point at which $\frac{dE}{d\theta} = 0$.

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*General.***3. The Effect of Temperature**

At normal or high temperatures the relations between the thermo-electromotive force of a thermo-couple and the difference between the temperatures of the hot and cold junctions‡ cannot be expressed by any general law or equation. In many cases, to a first approximation E may be regarded as varying linearly with θ over small temperature ranges, whilst to a higher degree of accuracy a parabolic law is in better agreement with the facts. Of these semi-empirical equations, one of the best known is that due to Avenarius,¹ which may be written in the form

$$E = at + bt^2$$

where t is the temperature in degrees centigrade. But this is to

* This point is discussed later; see page 202.

† The paper by Caswell (*Phys. Rev.* 1911, 33, 379) contains an interesting summary of much work in this connexion.

‡ In what follows we shall assume the cold junction to be at 0° C. unless stated otherwise.

be looked upon as purely empirical, and other equations have been suggested, although all are empirical in nature. Examples are:

$$E = a + bt + ct^2 + dt^3.$$

$$\log E = a + \frac{b}{t} + c \log t.$$

As regards the magnitude of the effect with pure metals, Pelabon² has investigated thermo-couples of many metals against platinum, and finds that the results can be expressed by relations of the type

$$E = \quad \quad \quad {}^2) \times 10^{-8}$$

where t is the temperature in degrees centigrade, and the constants a and b for the different metals are of the order $a = 10^2$ – 10^3 , whilst b is of the order unity. The thermo-electric power is thus of the order 10^{-5} – 10^{-6} , so that a thermo-couple of two normal metals gives an electromotive force of from 10^{-2} to 10^{-3} milli-volts (or 1–10 micro-volts), for a difference of 1°C .

If the thermo-electric powers of the different metals against some standard metal be plotted against the atomic numbers, no very definite periodic or other relationships appear to exist. Abnormally large values are shown by the borderline metals silicon, antimony, and bismuth, although the direction of the abnormality appears indefinite. With platinum as the standard metal the thermo-electric powers of silicon,* antimony, and bismuth at 0°C . are of the order +450, +50, and –70 micro-volts/ $^\circ \text{C}$. The alkali metals lithium, sodium, potassium, and rubidium, and also the magnetic metals iron, nickel, and cobalt, show abnormal values, although not to such a marked extent as in the case of the silicon or antimony, but again there appears to be no definite connexion between the abnormality and the Periodic Table. Thus with platinum as the standard metal, the thermo-electric powers of iron, cobalt, and nickel are of the order +20, –15, and –15 micro-volts/ $^\circ \text{C}$., whilst for the alkali metals the values are Li+14, Na–2, K–9, Rb–3, Cs+3. Taking the results as a whole one can only say that, at ordinary temperatures, the thermo-electric power between two pure metals very seldom exceeds 10 micro-volts/ $^\circ \text{C}$., but that marked exceptions are shown by the borderline metals silicon, antimony, and bismuth, and, to a lesser extent, by the alkali metals and by iron,

* The results for silicon are greatly affected by the exact purity of the specimen, and both highly positive and negative varieties can be prepared. (Fischer and Baerwind, *Z. Anorg. Chem.* 1913, 81, 243; 1916, 97, 56.)

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nickel, and cobalt. It seems to be quite certain that no simple connexion exists between the valency and the thermo-electric power of a metal at ordinary temperatures. Thus the thermo-electric powers of copper and zinc against platinum are almost identical, whilst cadmium is slightly more positive than silver, and mercury considerably less positive than gold.

Abnormalities in the Neighbourhood of the Melting-Point.

In most cases the semi-empirical formulae to which we have

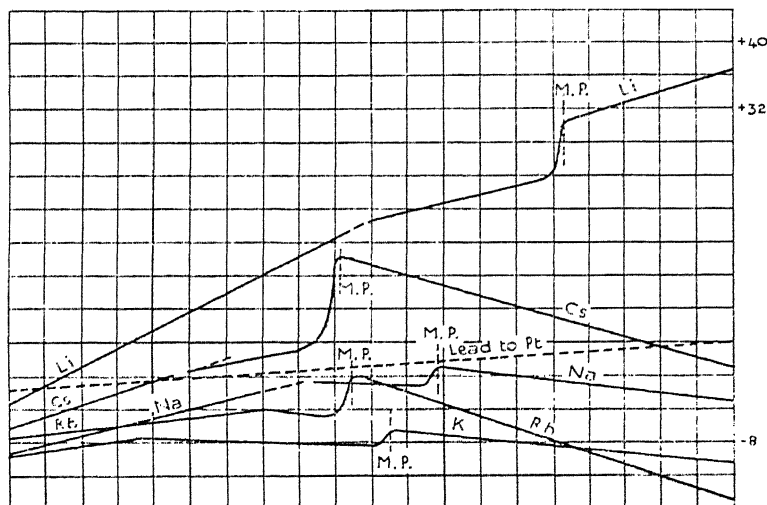


FIG. 27. Thermo-electric power of alkali metals against platinum.

referred cover the experimental data satisfactorily at ordinary or high temperatures, but with some metals an abnormal increase in the thermo-electric power is observed as the melting-point of the metal is approached. This phenomenon is particularly marked in the case of the alkali metals which have been investigated by Bidwell,³ whose results are shown in Fig. 27.

In this case the thermo-electric power curves for the solid metals show slight changes of direction at certain temperatures well below the melting-point, and this was taken by Bidwell as an indication of the existence of polymorphic transformations in these metals. Of much greater interest, however, is the fact that an abnormal increase in the thermo-electric power begins to occur about 10° below the melting-point, as can readily be

seen from Fig. 27. This abnormal increase in the thermo-electric power is accompanied by an increase in the resistance, and by a fading out of the X-ray diffraction patterns, although these are sharp at low temperatures. If the metals are pure, the melting-point is quite sharp, and the actual fusion takes place at constant temperature, but the changes in the electrical properties and X-ray diffraction patterns appear to indicate that a general loosening of the lattice occurs at least 10° C. below the melting-points.

With the alkali metals it will be seen that a distinct change in the direction of the thermo-electric power curves takes place at the melting-point. With other metals this change in direction is less marked although it is still observed. A point which may, however, at first seem puzzling is that if the thermo-electric *force* of a thermo-couple be measured with the hot-junction at increasing temperatures, no sharp break or discontinuity is observed when one metal melts. If, for example, one determines the electromotive force of a thermo-couple of platinum and lead with the cold junction at 0° C. and the hot junction at increasing temperatures, one obtains what is practically a smooth curve with a slight inflexion, but no sharp break or discontinuity when the hot junction reaches the melting-point of lead (327°). This, however, is due to the fact that in any such thermo-couple with junctions at two temperatures, there are two places where solid and liquid join. Thus if the lead wire be contained in a narrow glass tube with the platinum wire making contact at either end, and if the hot junction be above the melting-point of lead, there is not merely a junction of solid platinum-liquid lead, but also at some point in the tube containing the lead, there is a junction solid lead-liquid lead. As long as the hot junction is at the melting-point of lead, the presence of molten lead can have no effect on the thermo-electric force because it is simply equivalent to placing a new metal in the circuit, both junctions of the new metal being at the same temperature. By increasing the temperature of the hot junction above that of the melting-point of lead, we can obtain an indication of the difference in thermo-electric properties of solid and liquid lead, but, as we have already indicated, these differences are slight for most metals. Exceptions are, however, shown in the case of bismuth, where the thermo-electric power changes sign at the melting-point, so that there is a sharp break in the thermo-electric power curves. With accurate work there is always a break in the thermo-electric

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power curve at the melting-point, although, as in Fig. 27, this may often appear to be smoothed out if the observations are not made at sufficiently close intervals. But in the general case the break is slight, and it is one of the characteristics of the phenomenon that the thermo-electric powers of solid and liquid are nearly the same.

Effects at Low Temperatures.

In general very little systematic work appears to have been carried out on thermo-electric properties at low temperatures, and most experiments have been made in order to test conclusions based on the heat theorem of Nernst. According to this theorem, the thermo-electric power, $\frac{dE}{d\theta}$, should vanish at the absolute zero of temperature, so that the curves connecting E and θ should become horizontal at very low temperatures.

According to Onnes and Holst⁴ many disturbing effects are present when wires are used at the very low temperatures of liquid helium, but from measurements of the thermo-electric force of various metals against platinum they conclude that in the general case the E , θ curves become horizontal, so that the thermo-electric power vanishes, as the absolute zero is approached. An exception was shown by a thermo-couple of platinum and gold for which the thermo-electric power retained a finite value at 2.26° Abs., although a slight flattening of the curve was apparent. The more usual fall in the thermo-electric power in the region of the absolute zero naturally means that most thermo-couples are unsuitable for measuring the lower temperatures obtained by means of liquid helium.

At the slightly higher temperatures of liquid hydrogen (and also at the higher helium temperatures) the thermo-electric properties become considerably modified, and the exact relations between temperature and thermo-electromotive force become complex. In the case of the metals such as nickel and iron for which the thermo-electric power against the normal metals at ordinary temperatures is unusually high, the tendency, according to Wietzel,⁵ is for the thermo-electric power to diminish steadily as the temperature falls, and the same applies to thermo-couples of alloys, such as copper-constantan, which at ordinary temperatures have high thermo-electric powers. The exact relations are, however, complex and prevent many of these thermo-couples from being suitable at low temperatures. Thus Onnes

and Clay⁶ found it necessary to use a formula involving five constants in order to express temperatures in terms of the thermo-electromotive force of a copper-constantan couple, and even so the agreement was not always very good, although this thermo-couple, and also one of manganin-constantan, retained a sufficient thermo-electric power for them to be used at very low temperatures. A thermo-couple of silver and gold, on the other hand, although suitable at the higher temperatures obtained with liquid helium, could not be used at the lower helium temperatures.

Borelius, Keesom, and Johansson⁷ have investigated the Thomson effect in copper at temperatures down to -206°C . In this case the Thomson coefficient, which is positive at room temperatures, becomes zero in the neighbourhood of -140°C ., and then reaches a minimum value at about -180°C . As the temperature is lowered further, the curve for the Thomson coefficient rises steeply, the effect becoming zero again at about -195°C ., and then acquiring a large positive value at still lower temperatures. The same kind of variation was found in the case of silver alloyed with small amounts of gold, but in the case of an alloy of copper with a little gold the variation was more complex; the coefficient remained positive throughout, but first diminished to a flat minimum at about -140°C ., and then rose steeply to a sharp maximum in the region -230° to -240°C ., after which it fell rapidly to an almost zero value at -255°C . All these effects are thus very complex, and, as yet, comparatively little understood.

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4. The Effect of Pressure upon Thermo-Electric Properties

The thermo-electric properties of metals are affected by pressure although the underlying principles of the variation are not yet understood. The first work in this connexion is due to Wagner,¹ who used pressures up to 300 kg./cm.² at temperatures from 0° C. to 100° C., and concluded that the effect was a linear

function of the pressure within the limits of accuracy of the methods used. A more detailed investigation up to 12,000 kg./cm.² was made by Bridgman,² and, as this work confirmed the results of Wagner for low pressures, we shall refer only to these experiments.

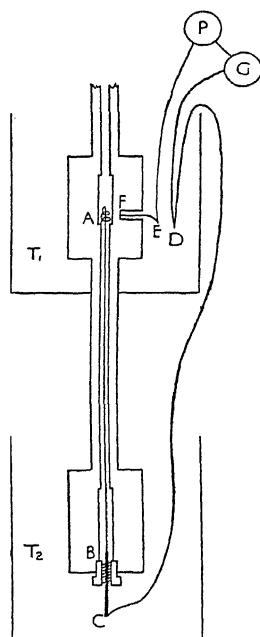


FIG. 28.

In this work the method used is to take a thermo-couple with wires made of the *same metal*, and then to compress one limb. The apparatus consists of two heavy cylinders *A* and *B* connected by a heavy tube, the two cylinders being kept at different temperatures T_1 and T_2 by means of thermostats, the lower temperature being 0° C. The wire to be examined runs through the tube but insulated from it. The wire is metallicallly connected to the inside of the upper cylinder, but passes out of the lower cylinder by means of an insulating plug of which a length of nickel steel *BC* forms the stem. The circuit outside the cylinder is completed by a wire of the same metal making connexion through

the insulating plug at the lower end, and directly with the steel cylinder at the upper end at *F*. The galvanometer (*G*) and potentiometer (*P*) are then joined by copper leads making contact at *E* and *D* which are kept at the constant temperature T_1 . The hollow cylinders and tube are then connected to the pressure apparatus. In this way the two places where there are stress changes, namely between *A* and *F*, and between *B* and *C*, are each in a thermostat, and thermo-dynamic reasoning shows that under these conditions the stress gradients can produce no electromotive force, so that the circuit simply gives the electromotive force of the uncompressed metal against the compressed.

In expressing the results, the following conventions are used. The thermal electromotive force of the circuit is called positive if the current flows from uncompressed to compressed metal at the hot junction, and the Peltier Heat is considered positive if heat is absorbed by the current on flowing from uncompressed to compressed metal. A positive $\frac{\omega E}{d\theta^2}$ means a larger Thomson Heat in the compressed than in the uncompressed metal, and as before the Thomson Heat is called positive if heat is evolved when the current flows from hot to cold.

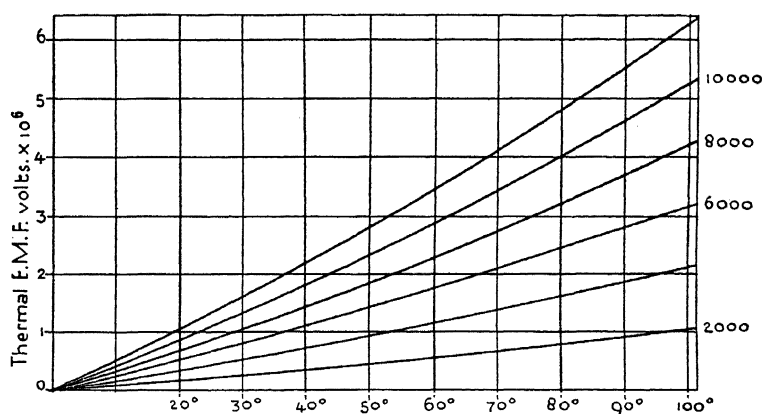


FIG. 29.

The figures at the end of each curve indicate the applied pressure in kg./cm.²

The general nature of the results obtained for most metals will be understood from Fig. 29, which shows the results obtained for lead. In the majority of cases the effect of pressure is positive, using the conventions as to sign described above. Exceptions are shown by magnesium and cobalt for which the effect is negative at all pressures up to 12,000 kg./cm.², and by iron, aluminium, and tin for which the results are much more complex.

The normal effect of pressure upon the Peltier Heat is also positive, that is to say heat is evolved by the current in flowing from compressed to uncompressed metal. This can be seen from the shapes of the lines in Fig. 29, but exceptions are shown by tin, magnesium, and cobalt.

The effect of pressure on the Thomson Heat is also generally positive, but exceptions are shown by cobalt, iron, and bismuth.

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The shapes of the curves connecting the Peltier and Thomson Heats at different temperatures and pressures are, however, very complicated and irregular, and it does not seem possible to express these variations in any general way.

As regards the magnitude of the effect, a pressure of 10,000 kg./cm.² produces a thermo-electromotive force of from 1 to 20 micro-volts for a difference of 100° C. between the hot and cold junctions, so that the change in thermo-electric power is about 0.01 to 0.2 micro-volts/° C. for 10,000 kg./cm.² or from 1×10^{-6} to 20×10^{-6} micro-volts/°C. 1 kg./cm.², but abnormally large values are found for bismuth.

In the case of the normal metals, the slope of the E.M.F. temperature curves at any given pressure increases with the temperature giving a positive value of $\frac{d^2E}{d\theta^2}$, and hence a positive

Thomson coefficient. At any given temperature of the hot junction the slopes of the E.M.F. pressure curves diminish with increasing pressure, so that the effect is not really a linear function of the pressure as was assumed by Wagner, the higher increments in pressure producing relatively less change. In the case of iron, aluminium, and tin, the temperature-pressure E.M.F. relations are however much more complicated.

Bridgman was unable to find any correlation between the effect of pressure upon the electrical resistance and thermo-electric properties of the different metals, and concluded that the thermo-electric effects were quite irregular and very complicated.

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5. The Effect of Deformation

The thermo-electric properties of metals are affected by deformation, and although the changes are small, they are relatively very much greater than those which deformation produces in the resistance. These changes are met with by many workers who use thermo-couples for accurate purposes, because the mere bending of the thermo-couple junction may alter the exact calibration. According to Neumann¹ the thermo-electric power may be as high as 2.6 micro-volts per ° C. for a thermo-couple of which the wires are of the same metal, but in which one wire is

rolled, and the other annealed. This figure is as high as the thermo-electric powers between many normal metals, and may serve to illustrate the danger from spurious effects which may arise in really accurate work unless the utmost precautions are taken. The sign of the thermo-electric power of the deformed against the undeformed metal is not always the same, showing that the effect is highly complex, and this was confirmed by Bridgman,² who investigated the electromotive force of thermo-couples of which the wires were of the same metal, but in which one wire was under tension, and the other not. In this case the effect of tension was to create an electromotive force between the stretched and unstretched wires, but the results were complex, and differed from one metal to another.

In general it may be said that the effects of deformation upon thermo-electric properties are but little understood, although the available data seem to make it clear that the conductivity and thermo-electric properties are affected quite differently.

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6. The (so-called) Homogeneous Thermo-Electric and Electro-Thermic Effects

In the preceding sections we have seen that when temperature differences exist at the junctions of a circuit of two metals, the Seebeck or Peltier electromotive forces are produced, and we may now consider whether any corresponding electromotive force can be obtained by temperature differences in a homogeneous circuit, made entirely of the same metal in the same condition. Unfortunately the experimental evidence on this point is very conflicting, and the different investigators are not in agreement. For many years the existence of such forces was considered to be impossible, and this conclusion was summarized in the Law of Magnus, according to which no thermo-electric currents can exist in a circuit of perfectly homogeneous metal, whatever may be the temperature distribution. In the course of the last fifteen years, however, it has been claimed by Benedicks,¹ that when a markedly unsymmetrical temperature gradient exists in a homogeneous circuit, a thermo-electric current is produced, as the result of the so-called *homogeneous thermo-electric effect*.

The experimental methods used in order to detect these effects

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are unfortunately open to considerable criticism. The general method employed in order to obtain a highly unsymmetrical temperature gradient is to heat bars or rods of metals in which one part is locally constricted as in Fig. 30.

In this case if the metal on one side of the constriction be heated, and that on the other be cooled, a very high temperature gradient must be produced in the narrow portion. An alternative method is simply to take two wires, and to lay the one across the other, forming the so-called 'thermo-electric cross' ('Drosselkreuz') in which the narrow point of contact gives a high temperature gradient when one of the wires is heated. Under these conditions Benedicks has shown that a difference of potential is produced, and may in some cases be as great as that of an ordinary thermo-couple. Thus with a thermo-electric cross of



FIG. 30.

tungsten wire with one limb near the junction heated to 900°C. , an electromotive force of the order 20 milli-volts could be obtained, and it was considered that the low conductivity of tungsten oxide made it improbable that an oxide film was responsible for the effect, although whether this conclusion is justifiable for a film of which the thickness is of the order of a few atoms is distinctly questionable.* Benedicks showed further that similar effects could be obtained with a platinum cross in which the wires were welded instead of merely being laid upon one another, and also by liquid mercury in a tube with a constriction.

Benedicks found that in all cases the sign of the homogeneous thermo-electric effect is the same as that of the Thomson coefficient of the metal concerned, positive Thomson coefficients in the case of copper and lead being accompanied by a positive thermo-electric effect; i.e. the hot wire of the thermo-electric cross acts as the positive pole if the two wires are joined to a galvanometer. This means that negative electrons flow from hot to cold across the steep thermal gradient at the cross.

The Homogeneous Electro-Thermic Effect. If the homogeneous thermo-electric effect really exists, it implies that a temperature

* It is to be noted that Bidwell has shown that some metallic oxides have remarkably high thermo-electric powers.

gradient in a homogeneous metal produces an electro-motive force just as an electro-motive force is created when the two junctions of a thermo-electric circuit are at different temperatures. In this case we may describe the thermo-electric effects by means of the following table:

<i>Effects.</i>	<i>The Metallic Circuit is</i>	
	<i>Homogeneous (1 substance).</i>	<i>Heterogeneous (2 substances).</i>
<i>Thermo-Electric Effects.</i>		
Heat Current Causes Electric Current	Benedicks (1916)	Seebeck (1821)
<i>Electro-Thermic Effects.</i>		
Electric Current Causes Heat Current	Thomson (1856)	Peltier (1834)

This scheme is not, however, entirely satisfactory, for the following reason. The Peltier Heat produced by the passage of a current across the junction of two metals is observed whether the circuit is initially at the same temperature or not, but, on the other hand, the Thomson Heat is only shown when there is initially a temperature difference in the conducting wire. Benedicks considered this to be anomalous, and therefore argued that just as the Peltier Effect takes place when the circuit is initially at constant temperature, so there should be a homogeneous electro-thermic effect as the result of which a current of electricity flowing down a conductor at uniform temperature should produce a transference of heat. This conclusion is in many ways rather striking, for it implies that if we take a perfectly homogeneous wire at constant temperature, and under absolutely uniform external conditions of cooling, &c., the passage of a current of electricity will not create a uniform rise in temperature owing to the Joule Heating Effect, but will produce a temperature gradient along the length of the conducting wire. In other words we can only have a steady state in which an electric current flows down a wire at constant temperature if we deliberately cool the wire in such a way that more heat is removed from some parts than from others.

The first experiments of Benedicks were carried out with a strangulated wire of the type shown in Fig. 31, thermo-couples being placed on opposite sides of the constriction. Under these conditions a temperature difference was observed which was

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proportional to the current density in the narrow portion (i.e. the current per unit cross-section), and proportional to the length of the constriction. In the same way when a current was sent through a thermo-electric cross with thermo-couples in thermal (but not electrical) contact with the ends (Fig. 32), a difference in temperature was observed which, as in the first experiment, was in the opposite direction to any effect to be expected from a spontaneous Thomson Effect due to the Joule Heating of the narrow portion.

All these methods were, however, clearly unsatisfactory, for if the homogeneous electro-thermic effect really exists



FIG. 31.

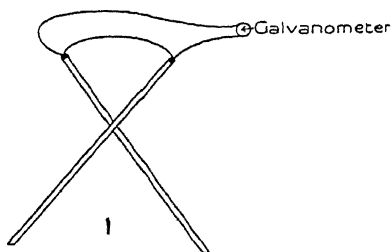


FIG. 32.

wire of uniform section, and the use of constrictions or crosses only serves to add an unnecessary complication. In a later paper Benedicks claimed to have confirmed the effect by an experiment in which a long length (500 cm.) of constantan wire was bent into a U-shape, and connected to copper leads, and the two junctions of a thermo-couple were placed in thermal contact with the ends,

but were insulated electrically. A current of 0.25 amperes was then passed through the long wire, and a difference in temperature between the ends was recorded, and was due chiefly to the Peltier effects between the copper and constantan, which served to produce heat at one junction, and to absorb it at the other. According to Benedicks, if the Peltier Effect were the only one acting, this effect must continually decrease as the thermo-couple junctions are moved uniformly towards one another from the ends of the long wire, and the effect should vanish asymptotically as the thermo-couple junctions approach one another at the middle of the wire. Actually, however, Benedicks found that the temperature difference vanished when the thermo-couple junctions were 380 cm. apart, the sign of the temperature difference then changing,

rising to a flat maximum, and sinking rapidly to zero as the thermo-couples approached one another in the middle of the wire. It was claimed that in this last case the temperature difference represented the pure electro-thermic effect and was proportional to the distance between the thermo-couple junctions, but this last conclusion was based on only a few observations, and appears distinctly questionable. It is to be noted that Benedicks's assumption of the temperature distribution if no homogeneous electro-thermic effect existed is not really justified, for, in the first place, the Peltier Effect itself depends upon the temperature, so that the heating and cooling effects at the two ends of the wire will be unequal as soon as the experiment has proceeded for a definite time, whilst apart from this the temperature gradient due to the Peltier effects at the two ends will make the resistance, and hence the Joule Heating Effect, vary along the length of the wire, although in the case of constantan this particular effect is probably negligible.

The Genuine Nature of the Homogeneous Thermo-Electric and Electro-Thermic Effects.

In the preceding pages we have described the claims of Benedicks that these so-called homogeneous effects are genuine, but it must be admitted frankly that many scientists consider that all of the phenomena are due to other causes such as strains in the wires, oxide films, &c. As regards the homogeneous thermo-electric effect there seems to be little doubt that the methods involving thermo-electric crosses, or locally constricted wires, are bad in principle, since the constrictions can only serve to introduce secondary effects. In this connexion a very interesting paper has appeared by Terada, Tsutsui, and Tamano,² who deliberately avoided the constriction principle, and used wires of uniform cross-section in which either a symmetrical or an unsymmetrical temperature gradient could be produced by means of suitable heaters. It was then shown that when wires of different metals were heated so as to produce an unsymmetrical temperature gradient, thermo-electromotive forces were produced, but that these underwent a *periodic fluctuation* as the position of the heater was moved along the wire. They then investigated the effect of symmetrical heating, and found that, as the heater was moved along the wire, a periodically fluctuating electromotive force was again obtained with copper, silver, and tungsten, although with aluminium this effect was smaller.

This 'symmetrical effect' was larger than any possible Benedicks Effect even if the latter did also occur with unsymmetrical heating. After discussing and examining various possible causes of the periodic symmetrical effect, the authors concluded that it must be due to the manufacturing process having produced a quasi-periodic fluctuation in the average orientation of the crystals along the wire, some preferred orientation remaining even after re-crystallization by annealing, since the symmetrical effect was found in annealed as well as in hard-drawn wire. In a later paper^{2a} it was considered that in some cases (e.g. nickel) the drawing process affected the surface of the wire, and that this was the cause of the effect. Whatever may be the correct explanation, these experiments are of great interest as showing the way in which spurious electromotive forces can be produced in what may appear to be entirely homogeneous wire heated perfectly symmetrically. They certainly throw great doubt as to the value of results obtained with constricted specimens.

As regards the possible effect of oxide films in connexion with the thermo-electric cross, Benedicks³ has examined the phenomenon in a high vacuum, and claims that the magnitude of the electromotive force is but little affected. Unfortunately the test was made with graphite, and not with a normal metal, and the readings themselves varied considerably with rising and falling temperature, so that the experiment is hardly conclusive for ordinary metals. The experiments with welded crosses are also unsatisfactory, since it is very seldom that welded metal has the same properties as the metal to which it is joined.

As regards the effect with liquid mercury it is to be noted that Benade⁴ could not detect a thermo-electromotive force in an experiment in which a temperature gradient of at least 600° C. per mm. was produced by means of an apparatus in which threads of mercury in hot and cold tubes were joined by a pin-hole in a sheet of mica. This investigator considered that the results of Benedicks were probably due to an ordinary thermo-electric effect between the mercury and the slate container. Tsutsui⁵ has obtained conflicting results with mercury in glass tubes, and also suggests that electromotive forces exist between the glass and the mercury. It is generally accepted that the presence or absence of the effect in a liquid metal is a crucial test, but it seems doubtful whether this is really so when constrictions and high-temperature gradients are involved, since convection currents and capillary phenomena may play a part.

On the whole, therefore, it can only be concluded that, considered purely from the experimental point of view, and neglecting theoretical considerations, the genuine existence of a homogeneous thermo-electric effect is at present 'not proven'. The strongest evidence in favour of the genuine nature of the phenomenon is the correspondence between the sign of the effect with that of the Thomson coefficient, although this has not really been tested for a large number of metals. But apart from this the position is very unsatisfactory, since the smallness of the electromotive forces makes it possible that they may be due entirely to secondary effects which have in all too many cases not been tested for critically.

For some curious reason, the so-called homogeneous electro-thermic effect has not aroused so much interest, although it is really just as fundamental as the homogeneous thermo-electric effect, since the electro-thermic effect implies that an electric current cannot flow down a wire without transporting heat. The first experiments of Benedicks with constricted specimens are clearly open to objection. In the case of the homogeneous thermo-electric effect, there was at least some justification for using constricted specimens in order to secure the necessary steep temperature gradient. But in the homogeneous electro-thermic effect, no initial temperature gradient is required, and the use of a constriction can only serve to introduce secondary phenomena. The later experiments with the long wire are of much greater interest, but, as we have already shown, the method is open to objection from one or two points, and as Bridgman⁶ has failed to confirm the experiment, a repetition with full testing for all possible secondary effects is much to be desired.

There is thus much scope for further examination of these most interesting effects, and it is to be hoped that a complete re-investigation will be made, since, from many points of view the phenomena are of fundamental importance. It is, however, essential that such an investigation shall be made with full attention to the numerous possible secondary effects, and that normal metals shall be investigated as well as the borderline metals such as bismuth or graphite. The work of Terada, Tsutsui, and Tamano, in which an investigation of unsymmetrical heating was accompanied by one of symmetrical heating, is a most excellent example of the way in which the problem should be attacked if the true answer is to be obtained.

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Annalen d. Physik, 1918, 55, 1-80, 103-50; 1920, 62, 185-217. These long papers contain an account of all the earlier experiments.

Homogeneous Electro-Thermic Effect.

Comptes Rendus, 1918, 167, 296; 1920, 170, 1382.

The Homogeneous Electro-Thermic Effect, Benedicks. Chapman & Hall, 1921. A general account in English is to be found in *J. Inst. Metals*, 1920.

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7. Results for Single Crystals

In the preceding sections we have referred only to the metals in their normal polycrystalline condition, but some thermo-electric properties of single crystals have now been investigated, and the results are of great interest. The first detailed work was due to Bridgman,¹ who examined the thermo-electromotive force against copper of single crystals of bismuth, zinc, cadmium, and tin. These experiments were, however, confined to a small temperature range, and a much more detailed investigation for zinc and cadmium was made later by Grüneisen and Goens,² whose results confirmed the general conclusions of Bridgman, although not the exact numerical values. The work of Grüneisen and Goens was carried out between the temperature limits -253°C. and $+100^{\circ}\text{C.}$, and their results at the higher temperatures agreed with some measurements on zinc crystals made by Linder³ at temperatures from 0°C. to 300°C. Grüneisen and Goens measured the thermo-electromotive force of copper against single crystals of different orientation, and then assumed that the thermo-electric power $\left(P = \frac{dE}{d\theta}\right)$ obeyed the symmetry relations of Voigt so that

$$P_{\phi} = P_{\parallel} \cos^2 \phi + P_{\perp} \sin^2 \phi$$

where P_{\parallel} and P_{\perp} are the thermo-electric powers parallel and perpendicular to the axis of symmetry, and P_{ϕ} the power in a direction making an angle ϕ with the principal axis. In this way

they calculated the thermo-electromotive force, the thermo-electric power, the Peltier Heat, and the difference between the Thomson heats for the two directions parallel and perpendicular to the principal axis in the single crystals of zinc and cadmium.

Fig. 33 shows the thermo-electromotive forces between the two principal crystallographic directions in this case, a positive sign

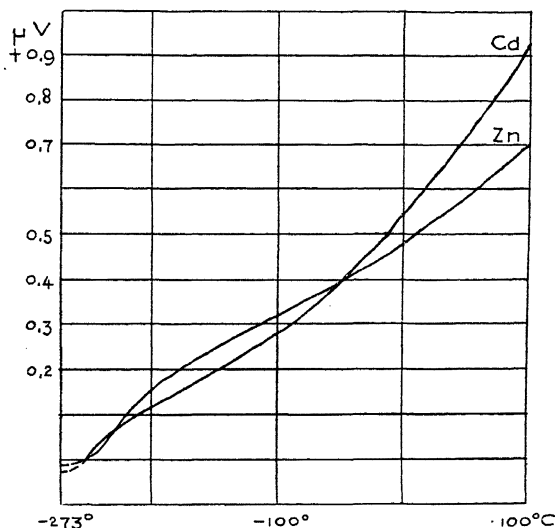


FIG. 33. Thermo-Electric Force between the two principal crystallographic directions in single crystals of zinc and cadmium. A positive sign means that the current goes from the parallel to the perpendicular direction at the hot junction.

meaning that the current goes from the parallel to the perpendicular direction at the hot junction. By drawing tangents to these curves, the corresponding curves for the thermo-electric powers can be obtained, and these are shown in Fig. 34, whilst Figs. 35 and 36 show the curves for the Peltier coefficient, and the difference between the Thomson coefficients. All these curves are characterized by marked fluctuations in the neighbourhood of -220°C. , which is the region where the atomic heats begin to decrease rapidly, and is also the temperature at which the ratios of the specific resistances $\frac{W_{\parallel}}{W_{\perp}}$ rise to a maximum.

In a later paper, Bridgman⁴ has investigated in great detail

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the applicability of the Kelvin-Voigt symmetry law to the thermo-electric phenomena. If the relation were fulfilled, the

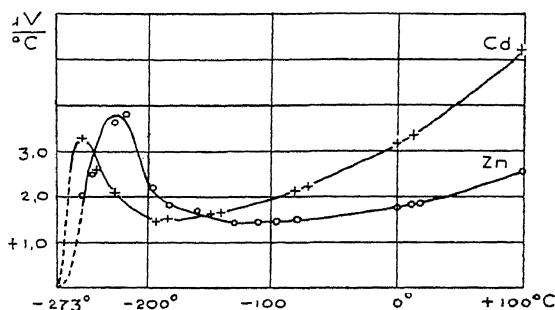


FIG. 34. Thermo-Electric Power $P = \frac{dE}{d\theta}$ between the two principal directions in single crystals of zinc and cadmium.

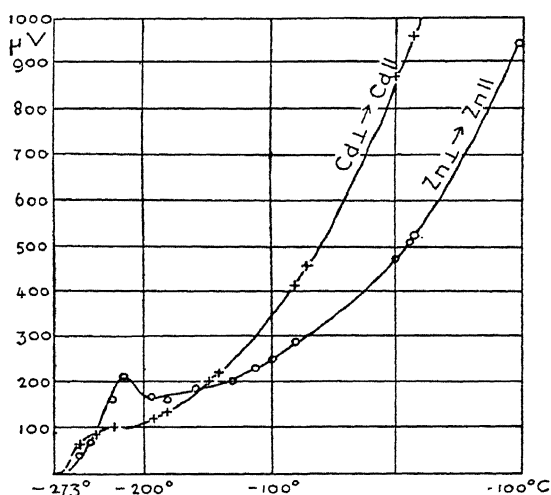


FIG. 35. Peltier coefficient between the two principal directions in single crystals of zinc and cadmium.

thermo-electromotive force of a single crystal against some standard metal should be a linear function of $\cos^2 \theta$, where θ is the angle between the axis of the specimen and the crystal axis. Using specimens of widely differing orientation, the linear relation was confirmed in the case of zinc, cadmium, and antimony, but with bismuth and tin there were deviations

greater than the probable error, so that the Kelvin-Voigt Law may really be an approximation only. But, on the other hand, in the case of bismuth, although the Kelvin-Voigt Law does not hold, the thermo-electromotive force still has rotational symmetry about the crystal axis. This point was not tested in detail for the other metals, but it is probably true for all crystals which have rotational symmetry. It was shown that within the experimental error of the methods, the Peltier Coefficient does not always obey the Kelvin-Voigt Law, and this was confirmed by the work of Fagan and Collins⁵ for single crystals of bismuth. For

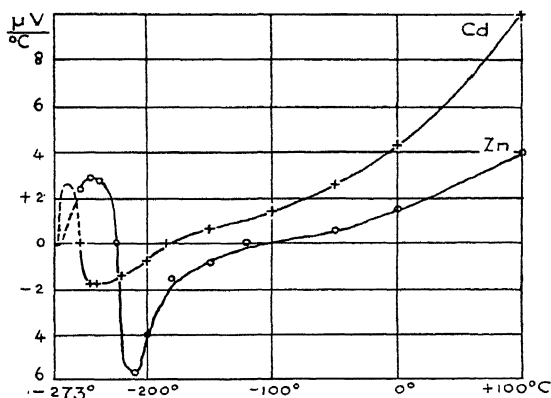


FIG. 36. Difference of Thomson coefficients $\sigma_{\perp} - \sigma_{\parallel}$ for single crystals of zinc and cadmium.

the Thomson Effect the possible error is greater since the second differential coefficient is involved, but it was concluded by Ware⁶ that for single crystals of zinc the Thomson Heat satisfied the Kelvin-Voigt Law, and this was in agreement with the work of Bridgman, although Fagan and Collins considered that a deviation might exist within the limits of accuracy of the experiments, but for the present this is unproved.

In crystals of this type, the two directions are thus profoundly different in thermo-electric properties, and if a thermo-couple were made with single crystal wires of one metal but of different orientations relative to the axis of the wire, the thermo-electric power would, in the case of zinc, cadmium, and tin, be of the same order as that between two different metals in the normal polycrystalline condition, whilst with single crystals of bismuth and antimony the effects are even more

striking. In the case of zinc and cadmium when the current passes from the perpendicular to the parallel direction heat is evolved, and the Peltier coefficient Π is positive. By a simple argument, Bridgman, and also Grüneisen and Goens, have shown that this must apply both when the change in direction of the current relative to the crystal axes takes place by a junction between two crystals of different orientation as in Fig. 37, and when there is a single crystal of such a shape that the direction of the current must change inside the single crystal as in Fig. 38.

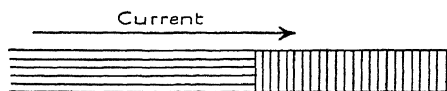


FIG. 37.

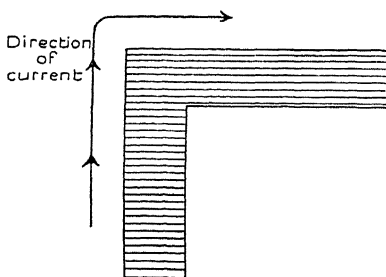


FIG. 38.

In other words, in these non-cubic crystals there is an internal Peltier Heat which is evolved (or absorbed) when the current changes its direction of flow relative to the crystal axes. In the case of antimony and bismuth these effects are remarkably large. Thus with antimony the Peltier heat $Sb_{\parallel} \rightarrow Sb_{\perp}$ is 0.0078 volts at 20° C., which means that one coulomb absorbs 0.0078 joules (7.8×10^4 ergs) in flowing from the parallel to the perpendicular direction. The

amount absorbed by one electron is therefore -1.24×10^{-14} ergs, whilst the energy of a gas molecule at 20° C. is 6.05×10^{-14} ergs, so that, in antimony, one electron in flowing from a direction parallel to the crystal axis to that at right angles to it evolves about one-fifth of the energy which it would have if it behaved as a gas molecule. In the case of bismuth the effect is about twice as great.

A further example of the differences between the thermo-electric properties in different directions in non-cubic metals is the so-called *transverse thermo-electric effect* predicted by Lord Kelvin as long ago as 1851,⁷ and lately confirmed experimentally by Borelius and Lindh,⁸ and by Bridgman.⁹ According to Lord Kelvin, 'if a bar of crystalline substance possessing an axis of thermo-electric symmetry has its length oblique to this axis, a current of electricity sustained in it longitudinally will cause

evolution of heat at one side, and absorption of heat at the opposite side, all along the bar, when the whole substance is kept at one temperature'. In the case of bismuth the effect is sufficiently large to be detected by quite simple experimental methods. In the work of Bridgman, a single crystal rod, of suitable orientation relative to the crystal axes, was set up so that a current could be passed through it, and temperature differences between the two sides of the bar were measured by a copper-constantan thermo-element with two junctions pressed by springs against opposite sides of the rod, but insulated from it by thin paper. Under these conditions a temperature difference of about 0.4°C . was observed with a current of 1 ampere in a rod of 10 mm. diameter. The effect was proportional to the current strength, and changed its sign when the current was reversed. The difference in temperature was a maximum at the two ends of the diameter lying in the plane perpendicular to the basal plane, and passing through the axis of the rod; the temperature difference reversed sign on rotating the rod through 180° , and vanished half way between the two orientations of maximum effect. The observations were independent of the longitudinal position of the thermo-couple relative to the rod, indicating that the whole of one side of the bar was warmed and the other cooled.

The same phenomenon was also detected in the case of single crystal rods of zinc, cadmium, and tin, but here the effect was very much less, being only about $1/500$ th of that for bismuth.

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8. Thermo-Electric Properties of Alloys

As in the previous chapters, we shall deal here with single-phase alloys only, and we shall consider primary and secondary solutions, and intermetallic compounds in one section because

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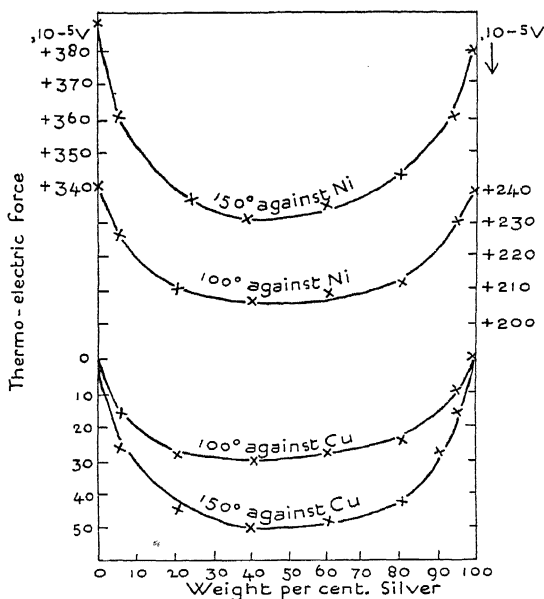
the available data are very slight. In the case of primary solid solutions the experimental methods consist in measuring the thermo-electromotive force of a series of alloys against a standard metal. For accurate work the measurements are made at small temperature intervals, and the E.M.F. temperature relation is plotted for each alloy against the standard metal, so that the thermo-electric power can be obtained as a function of composition. A more simple method is to measure the thermo-electromotive force of the alloys against the standard metal with hot and cold junctions at 0° C. and 100° C., and then to plot the E.M.F. against the composition of the alloy. In most cases the E.M.F. is almost a linear function of the temperature over small ranges, so that the simple method with junctions at 0° C. and 100° C. gives curves closely resembling those involving the true thermo-electric power, except that the unit is one hundred times greater.

In the case of primary solid solutions, when two metals are completely miscible in the solid state the relation between the composition and the thermo-electric power is expressed by a U-shaped curve. This is well shown in Figs. 39-40 which give the *thermo-electromotive force* of gold-silver alloys against nickel and copper, with hot junctions at 100° and 150° C., the cold junction being at 0° C. The true thermo-electric power $\left(\frac{dE}{d\theta}\right)$ curves are of the same general form since the E.M.F. temperature relations are nearly linear. These curves in some ways resemble those connecting conductivity and composition, but the resemblance is not exact, and, in general, the conductivity curves tend to have more steeply falling sides and flatter bases than the thermo-electric power curves. In other words, the first small amounts of a second metal in solid solution tend to affect the conductivity much more than the thermo-electric power.

Whether the solid solution alloy will be more useful for a thermo-couple than the constituent elements, depends entirely on the relative position of the metal which is to form the second wire of the couple. Thus, as can be seen from Figs. 39-40, if nickel be the second metal, the thermo-electric powers of both gold and silver are comparatively large and positive, and the alloys have smaller thermo-electric powers than their component elements. On the other hand with copper as the second metal, the thermo-electric powers of both silver and gold are comparatively small, and the alloys being negative would therefore form

more sensitive thermo-couples. But, at present, knowledge of this kind is empirical and cannot be predicted from the position of the elements in the Periodic Table.

The fact that there is no exact correspondence between the curves connecting the composition with the thermo-electric power, and with the electrical conductivity, is well shown by the work



FIGS. 39-40. Thermo-electric force of gold-silver alloys against copper and nickel (cold junction 0° C.; hot junction 100° and 150° C.), from the work of Rudolf.¹

of Norbury² who investigated the electromotive forces of thermo-couples in which one wire was of pure gold, silver, or copper, whilst the other was an alloy of the same metal with some other element in solid solution. From these results Norbury calculated the relative effect of one atomic per cent. of different elements in solid solution, but found that the order was quite different from the effect on the conductivity (see chapter II, page 44). With copper as the solvent metal, nickel caused a comparatively large negative effect to be set up by the alloy against pure copper, and the other metals followed in the order tin, aluminium, zinc, gold, and silver, the silver having a very small effect. Norbury

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pointed out that this order was that of the groups in the Periodic Table, VIII (Ni), IV (Sn), III (Al), II (Zn), and I (Au and Ag), but it is probable that this is rather a coincidence since the metals are from different periods. It seems, however, to be a regular rule that the three elements nickel, palladium, and platinum which immediately precede the univalent noble metals copper, silver, and gold have abnormal negative effects. But the chief value of this work is that it shows that there is no correspondence between thermo-electricity and conductivity.

In more complex alloy systems, the relations between thermo-electric properties and composition are at present little understood. According to Pelabon, when two metals form a simple eutectic series with no solid solutions, the thermo-electric power of the alloys against some standard metal is not a linear function of the composition, so that it is only natural that in more complex systems the results tend to become confused. In general the thermo-electric power-composition curves change direction at the composition at which a solid-solubility limit is reached, and we pass from a homogeneous to a two-phase alloy. As in the case of the liquid-solid change it is probable that there is a break or discontinuity in the thermo-electric power curve at transformation points, but in general the measurements have not been made at sufficiently close intervals for the break to be detected, and a change in direction is all that is observed. The thermo-electric power curves can thus be used for determining the phase-boundaries in an alloy system, although in many cases this method is not so suitable or sensitive as the more usual thermal, microscopic, or conductivity methods. Thus in the case of the β brass transformation, it has been shown by Matsuda that the change in thermo-electric power, although definite, is very slight indeed. But in some cases where the heat of transformation is small, and the conductivity method cannot be used, the thermo-electric methods are of value since, unlike the conductivity determinations, they are not seriously affected by flaws in the specimen.

Where intermetallic compounds are formed, the composition-thermo-electric power curves usually show slight cusps, but the factors affecting the actual values are little understood. Haken measured the thermo-electric power of many alloys against copper, and concluded that generally speaking compounds with low conductivities had high thermo-electric powers, but as many

of these were compounds of the borderline metals, bismuth, antimony, and tellurium, it is too early to say whether this is a general rule for all compounds of normal metals.

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VII

EMISSION PHENOMENA

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1. General

UNDER the heading of emission phenomena we shall include the various conditions under which metals can be made to emit electrons. Since most of the early work in this connexion has been described in other books, we shall not deal with the phenomena in detail, but as they have played an important part in testing the various theories of the metallic state, we shall give an outline of the subject for the benefit of those readers who may not be acquainted with the facts.

Broadly speaking, it may be said that a metal can be made to give off electrons by three methods which are generally sufficiently distinct for them to be considered separately, although under some conditions the processes may take place together.

In the first place, a metal will emit electrons if it be illuminated by light of a sufficiently short wave-length. This process is known as *Photo-Electric Emission*, and the general phenomenon is called *Photo-Electricity*.

Secondly, a metal will emit electrons spontaneously if it be heated to a sufficiently high temperature. This process is known as *Thermionic Emission*, and it is this which forms the basis of the thermionic valves used in wireless and other amplifying instruments.

Thirdly, a metal can be made to emit electrons if it be placed in a sufficiently strong electric field, and we may call this process the *Extraction of Electrons by Intense Fields, or Strong Field Emission*.

All these types of emission involve the escape of electrons through the surface of the metal, with the result that precise measurements are greatly influenced by numerous secondary effects due to variations in the exact surface conditions caused by surface films, adsorbed and absorbed gases, and other similar factors. Since in the present book we are concerned with the properties of metals themselves, we shall as far as possible omit the complications caused by secondary factors, and concentrate upon the results obtained with pure metals in high vacua.

Apart from their obvious practical value, these emission phenomena are of great interest in connexion with the ultimate structure of metals, because they give us some indication of the state in which the free electrons exist inside the metal, and thus enable us to test some of the theories which have been developed from other points of view.

General.

2. Photo-Electric Emission

When a piece of metal is illuminated by light of sufficiently short wave-length, it begins to emit electrons, and the chief points of interest are the relations between the intensity and frequency of the incident light on the one hand, and the number and velocity of the emitted electrons on the other. The principle underlying the experimental methods is comparatively simple, although the actual arrangements naturally involve many complicated details both as regards the electrical measurements, and the preparation of clean surfaces. The original method first introduced by Lenard consisted in placing the metallic specimen in a highly evacuated glass tube provided with a quartz window through which a beam of light could be thrown on to the metal. Opposite to the specimen was a small metal target, both specimen and target being soldered to platinum wires which were fused through the bulb. Let us now suppose that the metal is illuminated with light of sufficiently short wave-length to cause photo-electric emission. Electrons will then begin to escape from the metal specimen, and some of these will hit the target, and by suitable means we can measure the quantity of electricity, and hence the number of electrons which leave the specimen, and of those which hit the target. We may now apply a potential dif-

ference between the specimen and the target in such a direction that it tends to attract the photo-electrons back to the metal. If this potential difference be made sufficiently great, electrons will be unable to escape from the metal, and if no secondary phenomena are present to complicate matters, no electricity will pass from the specimen to the target. If the applied potential be gradually reduced, a point will be reached at which the photo-electrons with the highest emission velocities will just be able to reach the target, and the quantity of electricity passing in this way can be measured. If the potential difference be reduced to zero, and then applied in the opposite direction so as to help the electrons to escape, the number of electrons received by the target in unit time increases until a limiting value is reached, and the so-called 'saturation current' remains constant until very high potential differences are reached. This indicates that the actual emission process is practically unaffected by the small potential differences applied, and that the saturation current is attained when the potential is sufficiently great to overcome secondary effects such as collision with gas molecules, and so to enable all the emitted electrons to reach the target. This original simple apparatus has naturally been modified in many ways; thus in some cases the target is made of metal gauze, whilst in others the target is a silvered glass globe which completely surrounds the specimen except for the small hole admitting the light. But for these details reference should be made to the original papers.

In all these methods the results may be expressed in two different ways which may at first cause some confusion. In the first place we may describe a photo-electron in terms of its velocity, or by the corresponding kinetic energy, which, if we neglect the relativity correction, is given by $\frac{1}{2}mv^2$ if v is the velocity. Alternatively we may describe the electron in terms of the potential difference which must be applied in order to counteract the kinetic energy, and if V is this potential difference, the electron may be described in terms of 'equivalent volts' where $Ve = \frac{1}{2}mv^2$. For electrons with very high velocities this simple expression requires correcting in accordance with the principle of relativity.

Detailed tables connecting the velocity with the potential difference have been given by Fournier;⁷ and the following examples may be quoted in order to give an idea of the relative magnitudes involved.

<i>Electron Velocity in cm. per sec.</i>	<i>Kinetic Energy in Ergs.</i>	<i>Potential Difference in Volts.</i>
3×10^8	0.04×10^{-9}	25.44
9×10^8	0.36×10^{-9}	229
6×10^9	16.69×10^{-9}	10,490

There is, however, one further point which must be mentioned in order to avoid confusion when considering the experimental results. In the general type of apparatus to which we have referred, the measured potential difference is that between the metal specimen and the receiving target, and this potential represents the work which must be done on the emitted electron in order to prevent it from crossing the space between the specimen and the target, and from being received by the target. Consequently unless the specimen and the target are of the same metal, the observed potential differences require displacing by an amount equal to the contact difference of potential between the two metals, in order that the true potential corresponding to the velocity of the electrons may be obtained. In what follows we shall always assume that this correction has been made, unless it is expressly stated to the contrary.

The Photo-Electric Threshold Frequency.

One of the most striking facts in connexion with photo-electricity is that electron emission only takes place to an appreciable extent if the frequency of the incident light be greater than a certain limiting value, the so-called *threshold frequency*, the corresponding wave-length being called the limiting wave-length. If the frequency of the light be less than this limiting value, no emission will take place however great the intensity of the incident beam. In terms of the quantum theory this means that a definite minimum amount of energy must be given to the electrons in the metal before they are able to escape, and that the energy $h\nu_0$, corresponding to the threshold frequency ν_0 , represents this minimum energy, h being Planck's constant. It is naturally a matter of interest to see whether the threshold frequencies of the different metals can be connected with their positions in the Periodic Table, or with any other physical or chemical properties, but unfortunately the results of different workers are frequently so much at variance that comparisons are very dangerous, since the relative orders can often be altered by picking and choosing results from different sources. Apart from this difficulty, it has been shown by Richardson¹¹ that in

some cases at any rate, there appears to be more than one threshold frequency, a result ascribed to the existence of patches of the metal surface in different states.

In all cases, however, the threshold frequency of an alkali metal is less than that of the alkaline earth metal which follows it directly in the Periodic Table, and when the threshold frequencies are plotted against the atomic volumes, the two groups of metals appear to separate themselves into two curves as will be seen from the following figure. In this case, where results differ, we have adopted the policy of taking the lowest value of the threshold frequency, or the largest value of the limiting wave-length, since it seems to be generally recognized that with reactive metals such as these, the presence of surface films prevents the escape of electrons, and so tends to make the apparent threshold frequency too great.

In view of the later theories of the structure of metals it is naturally tempting to see whether this method can be used to determine the number of free electrons per atom which are present in the different metals, since it is very probable that the atoms are definitely ionized, and in this case we may expect the ease with which an electron can escape from the metal to depend chiefly on the volume and the degree of ionization, so that if the threshold frequency be plotted against the atomic volume, the points may be expected to separate themselves into groups corresponding to the different degrees of ionization, variations caused by factors such as the crystal structure being supposed comparatively slight. In the case of the alkali and alkaline earth metals this separation into groups is confirmed, and it is interesting to note that aluminium seems to fit on to the curve of the univalent alkali metals, a fact which may be in agreement with the now generally accepted theory of atomic structure, according to which the three valency electrons of the normal aluminium atom are not equivalent, but consist of two electrons in (2, 1, 1) orbits and one single electron in a (2, 2, 1) orbit.*

But in other cases the results of different workers are frequently so much at variance that comparisons of this kind cannot be made, especially where the atomic volumes are small, so that the points lie near the origin. It seems, however, to be clear that, in contrast to the change on passing from alkalis to the alkaline

* As we shall see later (p. 323), the evidence from the crystal structures and melting-points supports the view that in solid aluminium the atoms are not fully ionized to the 3-valency limit.

earth metals there is no marked fall in the long wave-limit on passing from the univalent metals copper and silver to the following divalent metals zinc and cadmium [Cu, 3000 Å°, Zn

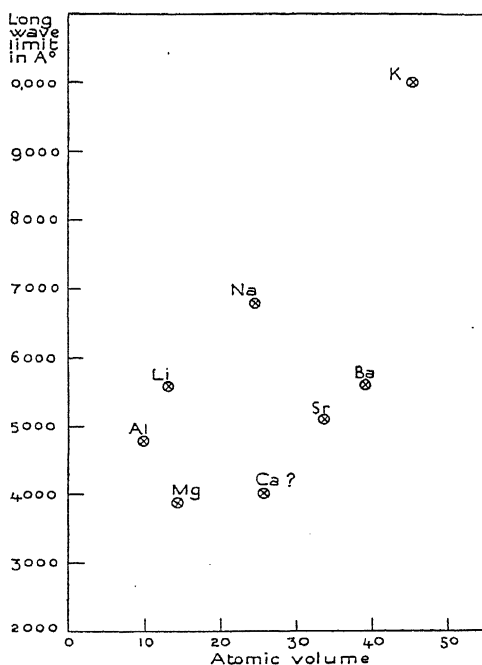


FIG. 41. Showing the Photo-Electric Long Wave-Limit plotted against the Atomic Volume. *Note.* The value for calcium is uncertain, as the specimen was cleaned in air and the metal is very reactive. The values for potassium obtained by different workers also vary greatly, possibly owing to the presence of multiple thresholds. These variations do not, however, affect the general rule that the long wave-limit is much greater for an alkali metal than for the alkaline earth metal which follows it directly in the Periodic Table.

3000–3700 Å°; Ag 3390 Å°, Cd 3140 Å°]; the theoretical significance of this will be discussed later. In some cases doubt exists as to whether the threshold frequency of a metal is really a characteristic of the metal, or whether it varies so much with the exact conditions as to make the actual numerical values of little or no value. There is no doubt that in the earlier work the apparent variations in threshold frequency were due to chemical action and surface contamination, but in the much more accurate work of Millikan,⁵ in which fresh surfaces of the alkali metals were

cut in a vacuum, it was found that the sensitivity and threshold frequency changed considerably with time, and that the direction of the change varied with the wave-length of the incident light. Variations with time were also found by Welch,¹⁵ in whose work fresh surfaces of different metals were prepared in a vacuum by a magnetic filing device. Up to the present these changes have been considered as entirely due to chemical action between the freshly cut surface and the traces of gas remaining in the vacuum tube, but it is also possible that physical changes may affect the results, since the cutting of a metal produces abnormal conditions at the surface, and although the exact nature of strained metal is still obscure, there is no doubt that with soft metals of low melting-point spontaneous recrystallization takes place at room temperatures, so that a gradual change in the properties of a freshly cut section is only to be expected. At present therefore, the numerical values of the threshold frequencies have seldom much significance as exact characteristics of the metals, although the wide differences between certain metals, such as for example the alkali and alkaline earth groups, may be considered as quite definitely established.

The Effect of Wave-Length upon Photo-Electric Emission.

In the preceding section we have seen that photo-electric emission only takes place if the frequency of the incident light exceeds a certain limiting value, but if once this value be exceeded there is a comparatively simple relation between the frequency of the light and the maximum velocity of the photo-electrons. This relation is given by the well-known equation of Einstein, which may be written in the form

or alternatively

$$\frac{1}{2} m v^2 = h \nu - P$$

where ν is the frequency of the incident light, and ν_0 is the threshold frequency. The validity of this equation was tested by Richardson and Compton,¹⁹ and by Hughes,¹⁶ and also in great detail by Millikan,¹⁷ who prepared freshly cut surfaces in a vacuum for specimens of the alkali metals, and it was shown that the equation held with such accuracy that the method could be used for the determination of Planck's constant h . Expressed in terms of most of the modern theories, the factor P (or $h\nu_0$) represents the least amount of energy which must be given to

the electrons which are most ready to escape, in order that they may break through the surface of the metal. It should be noted that the Einstein equation applies not only to radiation of which the frequency is within the visible or ultra-violet region, but also to radiation of much higher frequencies, such as X-rays or the γ -rays from radioactive substances.

In general therefore the energy of the photo-electrons of maximum velocity varies linearly with the frequency of the incident light, and if the straight line thus obtained be extrapolated it cuts the frequency axis at a value ν_0 equal to the threshold frequency.

The above remarks refer to the photo-electrons of maximum velocity, but the velocities are really distributed over the whole range from zero to the maximum value, and we have therefore to consider this nature of the velocity distribution. This problem was investigated in detail by Richardson and Compton, and their results in the case of platinum are shown in Fig. 42. In this figure the abscissae represent the electron velocities in equivalent volts, whilst the ordinates give the distribution. Thus for the curve corresponding to light of wave-length 23λ ,* the number of electrons with velocities 0.2 equivalent volts is to the number with velocities 0.7 equivalent volts, as the ordinate at 0.2 is to the ordinate at 0.7, i.e. as 3 : 2. These curves are almost symmetrical, and consequently, since the maximum energy varies linearly with the frequency, the average energy, which is also the most probable energy, must vary linearly with the frequency. The same general types of distribution curves were shown to hold for all metals.

We have next to consider the effect of frequency upon the total photo-electric emission, that is to say the total number of photo-electrons which are emitted irrespective of their velocities. The first work in this connexion, except for some experiments by Pohl and Pringsheim on the so-called selective effect referred to below, was carried out by Richardson and Compton, who showed that the same general relations held for most metals, and that when the total photo-electric current was plotted against the frequency, the curves rose to a maximum at a particular frequency $\nu_{\max.}$, which was connected with the threshold frequency ν_0 by the simple relation $\nu_{\max.} = \frac{3}{2} \nu_0$. These same general conclusions have been confirmed in later work by Richardson and Young,²⁴ Döpel,²⁵ and Roy,²⁶ all of whom obtain the same general types of frequency-emission curves, although for some

* The unit of wave-length λ is here 10^{-6} cm.

metals the values of ν_{\max} are too far in the ultra-violet for measurements to be made. For some of the alkali metals the frequency-emission curves rise to two maxima, corresponding to two values of ν_{\max} , and consequently indicating two values of ν_0 , a result which, as we have already seen, is ascribed by Richardson

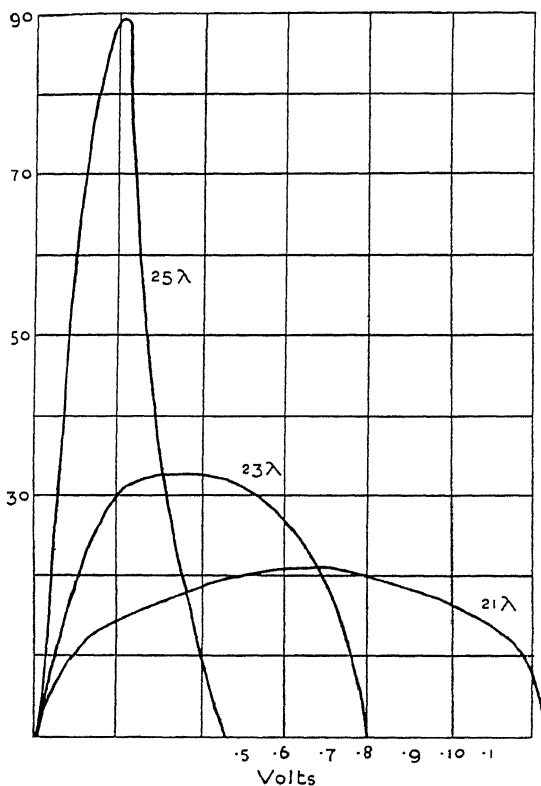


FIG. 42.

to the existence of the metal in two distinct states. For the general case in which the frequency-emission curves show one maximum only, we have the simple relation

$$F_{\nu} = \frac{3}{2} \nu_0 \nu$$

If, therefore, F_{ν} represents the number of electrons emitted by the absorption of unit quantity of radiation of frequency ν the above relation is satisfied if F_{ν} be of the form

since this rises to a maximum when $\nu = \frac{3}{2}\nu_0$. An expression of this kind represents most of the main features of the relations between emission and frequency, although the shape of the theoretical curve does not always agree exactly with that determined experimentally, but at present satisfactory data on metals completely free from gas are very scanty.

The above results refer exclusively to normal polycrystalline metals, and at present there is little evidence as to the effect of crystal structure upon the photo-electric emission. According to Parnley,²⁷ the emission from a single crystal of bismuth on which a fresh face was cut *in vacuo*, was indistinguishable from that of a polycrystalline specimen prepared in the same way, in spite of the fact that the crystal structure is not cubic, and that the electrical conductivity varies with the orientation. On the other hand, according to Linder,²⁸ a single crystal of zinc showed distinct variations in the photo-electric emission as the crystal was rotated, the current when the illuminated surface was normal to the hexagonal axis being about twice that when it was parallel. In this case, however, the surface was cleaned by evaporation, and consisted of a number of microscopic crystal facets, so that a secondary factor may have been introduced, and further work on the properties of single crystals is undoubtedly called for.

The Effect of Intensity of Illumination upon Photo-Electric Emission.

In the preceding sections we have seen that, however powerful the light, no photo-electric emission takes place if the frequency of the incident light be less than the threshold value, but, once this limit is reached, there is a very simple connexion between the intensity of the light and the number and velocity of the emitted electrons. This relation may be summarized by saying that for light of a given wave-length, the number of emitted electrons is directly proportional to the intensity of the light, but their velocities are quite independent of the intensity. This very remarkable result was first obtained by Lenard,⁶ and has since been confirmed by many investigators, but as this work has been described fully elsewhere we shall not deal with it further here.

The Effect of Temperature upon Photo-Electric Emission.

The large amount of work which has been carried out on the effect of temperature upon photo-electric emission may be sum-

marized in one sentence by saying that when secondary effects due to absorption of gases, formation of surface films, &c. are eliminated, the photo-electric process is practically unaffected by temperature up to the point at which thermionic emission begins, when the two processes take place together.

This comparatively simple conclusion was only reached after much work, and many apparently contradictory results. The reason for this was that most of the earlier investigators did not carry out their experiments in a high vacuum, and consequently their results were complicated by a number of secondary processes affecting the exact condition of the surface. The earliest really satisfactory work in this connexion was due to Millikan and Winchester,²⁹ who first showed that, when aluminium in a high vacuum was exposed to ultra-violet light from zinc electrodes, the photo-electric emission and potential difference acquired were independent of temperature within the range 50° C. to 343° C. These investigators also examined ten other metals in the range 25° C. to 125° C. and were led to the same conclusion, and identical results were obtained independently at about the same time by Ladenburg,³⁰ who examined the photo-electric effect in gold, platinum, and iridium at temperatures from 20° C. to about 800° C., and concluded that when secondary effects due to the occlusion of gases and water-vapour were avoided, the process was quite unaffected by temperature up to the point at which the metals begin to emit electrons spontaneously (thermionic emission), when further measurements became impossible. In general these conclusions have been confirmed by later workers for both high and low temperatures, although there is some slight confusion as to whether prolonged heat treatment at very high temperatures may not reduce the photo-electric effect very greatly in the case of some metals such as platinum. According to Wiedemann and Hallwachs,³¹ and other investigators, whilst adsorbed surface films of gases hinder the process of photo-electric emission, the presence of small quantities of absorbed gases within the metal may greatly increase the emission, and their removal by prolonged heating at very high temperatures may render the metal almost inactive, but later work by Tucker,³⁴ Woodruff,³³ Velo,³⁵ and DuBridge³⁶ has shown that the effect is due to a shift of the threshold frequency towards the ultra-violet, to a value below the shortest line furnished by the usual quartz mercury arc, and that if shorter wave-lengths are used, the metal retains a definite activity.

In the general case, therefore, the process of photo-electric emission is to be looked upon as independent of temperature, provided that the metal does not undergo a transition in the temperature range considered. But in the case of iron, where transitions occur as the temperature is raised, it has been shown by Cardwell³⁷ that there is an abrupt decrease in the photo-electric current when the iron changes from the α , body-centred cubic form, to the γ or face-centred cubic variety.

It has been shown by Ives³⁸ that in the case of the alkali metals a slight shift in the threshold frequency occurs at the low temperatures which can be reached by means of liquid air (-180°), but it is not yet known whether this is the case for all metals.

Miscellaneous Effects.

In the preceding sections we have only described the simplest forms of photo-electric emission, and there are also additional and more complicated details, but since these have so far contributed little or nothing to our knowledge of the ultimate structure of metals, we shall only refer to them briefly. The first of these complications is the so-called 'selective photo-electric effect', which becomes apparent when some metals are exposed to the action of polarized light. We have already seen that when ordinary unpolarized light falls upon a metallic surface, the photo-electric emission rises to a maximum at a particular frequency ν_{max} , which is connected with the threshold frequency by the relation $\nu_{\text{max}} = \frac{3}{2} \nu_0$. But whilst in the great majority of cases the emission is independent of the state of polarization of the light, there are some metals, such as those of the alkali group, in which the emission over a certain range of wave-lengths is many times greater when the light is polarized so that the electric vector has a component parallel to the plane of incidence, although the maximum velocity of the emitted electrons is independent of the orientation of the plane of polarization. This effect is confined to a certain range of wave-lengths, and rises to a fairly sharp maximum at a particular frequency, the so-called 'characteristic frequency of the selective effect', but the Einstein relation between the frequency of the light and the velocity of the emitted electrons is still obeyed. The cause of this effect is obscure, and it is usually regarded as due to the coincidence of the particular frequency of the light with some characteristic frequency of the metal.

An interesting phenomenon in connexion with photo-electricity was discovered by Shenstone,³⁹ who found that the photo-electric emission was increased if an electric current were passed through the emitting metal. In the case of bismuth if the current through the specimen be gradually increased, the photo-electric emission passes through a maximum, and finally falls below its initial value, and if the current be then stopped, the emission slowly retraces the original curve, rising to a maximum and then sinking to the initial value. In the case of copper, however, the emission increases continuously with the current, and when the latter is stopped the emission slowly returns to the original value. Careful experiment showed that the small heating effect of the current could not be responsible for this phenomenon, the cause of which is unknown.

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3. Thermionic Emission

General.

The second method by which metals can be made to emit electrons is by heating to a sufficiently high temperature, and it is this process which forms the basis of the various thermionic valves which are used in so many connexions. As in the case of photo-electricity, the early study of thermionic emission was complicated by many secondary factors due to the presence of a gaseous atmosphere, surface contamination, impurities, and similar effects, and it was only after experiments carried out in a vacuum that the process could be examined as a characteristic of metals themselves. Considerable confusion was caused at first by the discovery that under certain conditions some metals would apparently emit positively charged particles at low temperatures, but that, as the temperature was raised, negatively charged particles were emitted in a continually increasing proportion. As a result of much careful work it was shown by O. W. Richardson that the positive emission was in general a temporary phenomenon which decreased with continued emission, and was due to the presence of impurities, particularly of the alkali metals or their compounds. On the other hand the negative emission was a permanent and reproducible process, and it was first shown by J. J. Thomson in 1899 that this emission was due to the particles of negative electricity which we now know as electrons.

The chief interest in the process lies in the relations existing between the temperature and the emission on the one hand, and

in the velocity distribution of the emitted electrons on the other. The experimental methods are comparatively simple in principle, although there are naturally many complicated details in connexion with the removal of impurities, and the avoidance of secondary effects. In the general type of apparatus, a wire or filament of the metal which is to be examined is placed along the axis of a hollow cylindrical metal electrode, the whole being sealed into an evacuated glass vessel. The filament is then heated by the passage of an electric current, and when electrons begin to be emitted some of them reach the cylindrical electrode, and the current flowing between the filament and the electrode can be measured. This current does not, however, correspond with the total number of the emitted electrons, since some of these may be deflected back to the filament owing to various secondary effects such as collision with gas molecules, mutual repulsive action of the emitted electrons, the positive charge on the metal, the effect of the electric current in the filament, and other factors. In order to obtain the total emission, a potential difference is applied between the filament and the electrode in such a direction as to help the emitted electrons to cross the intervening space, and it is found that, as this potential difference is increased, the emission current, in a high vacuum, at first increases approximately linearly with the potential, but then reaches a limiting value, the so-called 'saturation current', which remains constant over a considerable range. This indicates that the actual emission of electrons, as in the photo-electric process, is practically unaffected by small potential gradients, and that the saturation current is reached when the potential gradient is sufficiently great to overcome the secondary phenomena, and thus to enable all the emitted electrons to reach the cylindrical electrode, and it is only in cases where this saturation limit can be reached that the total number of emission electrons can be measured. As in the case of photo-electric measurements, the velocities and velocity distribution of the emitted electrons can be determined by varying the potential difference between the filament and the electrode.

The Effect of Temperature upon Thermionic Emission.

The actual values of the emission currents obtained from any metal at a particular temperature vary greatly with the exact conditions, but the general characteristics of the process are now well established. In most cases the emission currents are

too small to be measurable at temperatures below about $1000^{\circ}\text{C}.$, although with the alkali metals the effect is noticeable at much lower temperatures. As an indication of the general results obtained, reference may be made to Fig. 43, which is taken from the work of Langmuir,³ and shows the emission currents obtained from tungsten at various temperatures with potential differences of 60, 120, and 240 volts between the filament and the cylindrical

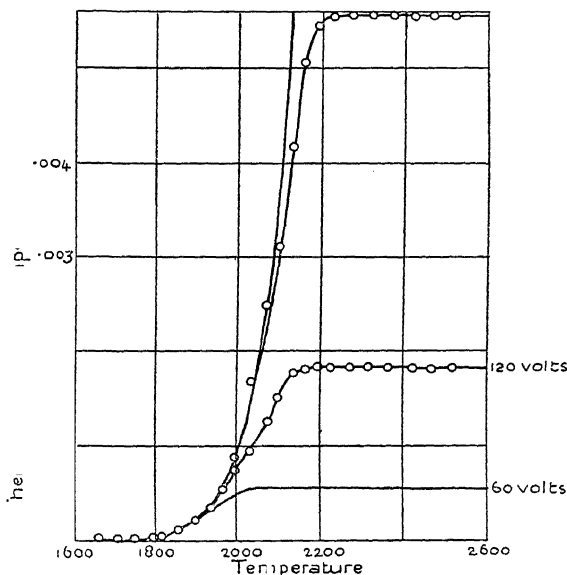


FIG. 43.

anode. From this figure it will be seen that the three curves coincide up to a temperature of about $1900^{\circ}\text{K}.$, above which the curves separate, and a state is reached at which the current for a given potential difference becomes independent of temperature, and it was shown by Langmuir that this flattening off of the curves was due to the repulsive action of the electrons upon one another. This 'space-charge' effect is only important at extremely high temperatures where the emission becomes so large that the mutual repulsion always drives some electrons back to the filament, so that the total emission can never be measured with the voltages usually employed. Under these conditions the saturation current is never reached, but at lower temperatures this difficulty does not arise, and the true total emission can be measured.

The chief characteristic of the relation between temperature and emission is that above a certain point the emission increases very rapidly. The numerical results can be expressed satisfactorily by various exponential equations, and of these the best known is that of Richardson, which, as we shall see later, can be deduced theoretically by arguments based on the older electron-gas theories. This equation is of the form

$$I = A\theta^{\frac{1}{2}}e^{-\frac{b}{\theta}} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where b is the so-called thermionic work function and is proportional to the work which the electron has to do in order to cross the surface. In the simpler theory b is assumed to be independent of temperature, and is equal to $\frac{\phi}{k}$ where ϕ is the work done in crossing the surface, and k is the Boltzmann constant. It has been shown by Richardson,¹ and K. K. Smith,² that, with suitable values of A and b , this equation covers the numerical data over a very wide range of temperature and current strength, but unfortunately the relative influence of the exponential term is so great that other formulae are equally satisfactory. An alternative equation which, as we shall see later, probably has a better theoretical basis is of the form

$$I = C\theta^2e^{-\frac{d}{\theta}} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where C is, theoretically, an absolute constant for all metals, and, according to the simplest form of the theory, should equal 60.2 amp./cm.²/deg. or 1.81×10^{11} in electrostatic units.* A general idea of the magnitudes involved may be gained from Table XXVIII, which is taken from the work of Richardson. In

TABLE XXVIII

Metal.	Equation 1.		Equation 2.		Volts.
	A	b	C	d	
Platinum	10^{26} to 10^{31}	5×10^4 to 8×10^4	10^{19} to 10^{18}	5×10^4 to 8×10^4	4 to 6.6
Tungsten	10^{26} to 10^{27}	5.2 to 5.5 "	1.9×10^{11}	4.9 to 5.2 "	4.25 to 4.5
Tantalum	10^{21} to 10^{28}	4.4 to 5.0 "	10^4 to 10^{11}	4.2 to 4.7 "	3.5 to 4
Calcium	10^{28}	3.6 "			

this table the values of A and b in equation (1), and of C and d in equation (2), have been calculated, the current strength being expressed in electrostatic units. The last column gives the potential differences in volts which, according to the theory employed,

* In the later theories of Sommerfeld and Nordheim (Chapter XIII), the theoretical value is 120, and not 60.

are equivalent to the energy change experienced by the electron in escaping through the surface of the metal; it will be seen that these vary from 3 to 7 volts, and this is the general order of magnitude for most metals.

It will be noted that the values of the factor C in equation (2) are very far from being constant, and that it is only in the case of tungsten that the theoretical value of 1.8×10^{11} is approached. The question of this variation has been discussed by many investigators, but the results are at present inconclusive. It was first claimed by Dushman,⁴ in 1924, that the emission data were in agreement with the theoretical value of C (60) in the case of pure tungsten, molybdenum, and tantalum in a high vacuum, and this was confirmed by Zwikker⁵ for tungsten, molybdenum, and thorium, but not for hafnium or zircon. It has, however, been shown by DuBridge⁶ that when all traces of gases are removed from platinum, the metal reaches a steady state in which the value of the constant C is 250 times greater than the theoretical value, although in other respects the metal behaves in agreement with theory. The position is thus uncertain as regards pure metals, whilst in the presence of gases it appears quite certain that the value of C is not that required by theory.

From many points of view these equations are, however, very unsatisfactory for comparison with the experimental data, because a small variation in the terms b or d may counterbalance a change in the terms A and C , so that by suitably adjusting the constants the equations may be made to fit the facts. The values for the terms b and d , obtained by different investigators for the same metal, are usually in agreement within 10 or 20%, but this variation again prevents them from being used critically as constants characteristic of the metal, so that except for a few metals the present values for the thermionic constants are so much affected by secondary factors as to be of little value as characteristic constants. On the other hand, the general nature of the emission-temperature variation is always the same, so that with a given metal in a given condition as regards contamination, gas-pressure, &c., the emissivity data can be expressed accurately by equations such as (1) and (2) provided that suitable values are given to the constants.

The Velocity Distribution of Thermionic Electrons.

The first measurements of the kinetic energy and velocity distribution of electrons emitted from hot metals were made in

1907-9 by O. W. Richardson and F. C. Brown,⁷ who concluded that the velocity distribution agreed with that required by Maxwell's Law of distribution for a gas composed of particles with a molecular weight equal to that of an electron, in thermal equilibrium at the temperature of the emitting wire. This conclusion was confirmed in 1914 by the work of Schottky,⁸ who found that the velocity distribution was in agreement with the Maxwell Law, except that the average kinetic energy was greater than that required theoretically. Both these investigations were, however, open to certain criticisms, and a more detailed investigation was made in 1922 by J. H. Jones,⁹ who examined the emission from tungsten at temperatures from 1500° to 2000° Abs. If the velocity distribution of the emitted electrons be that required by Maxwell's Law, it can be shown that the current flowing between two parallel plates under a potential difference V is given by the relation

$$I = I_0 e^{\frac{Ve}{k\theta}}$$

where I_0 is the saturation current, and k is Boltzmann's constant. For electrodes of different shape, this expression requires modification, but in any case the relation is such that if $\log I/I_0$ be plotted against V , a straight line should be obtained of which the slope can be calculated. It was shown by Jones that for tungsten in a good vacuum the results were in agreement with the Maxwell Law, although, owing to the difficulty of measuring small currents, and also to various secondary effects, the possible error was of the order 10 to 20%.

The same general conclusion was reached in 1923 by H. H. Potter,¹⁰ who investigated the emission from platinum in a high vacuum, and showed that the mean slope of the $(\log I, V)$ curves from thirteen experiments was 2.68 as compared with the value 2.72 required by Maxwell's Law at the temperature of 1450° C. But when traces of hydrogen were present, although the linear relation still held between $\log I$ and V , the average energy of the electrons was higher than that demanded by theory. This was confirmed by J. F. Congdon,¹¹ who showed that the electrons emitted from tungsten in a high vacuum had velocities in agreement with the Maxwell Law, but that their energy was increased if small amounts of hydrogen were present, although traces of argon had no effect. Similar results have been obtained by Germer¹² and others, and it may now be taken as established that within the limits of the experimental methods the electrons

emitted from pure metals in a high vacuum have velocities in accordance with the Maxwell Law, but that in the presence of some gases the velocities are altered, although the linear relation between $\log I$ and V is still maintained.

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4. The Extraction of Electrons by Intense Fields

The third means by which a metal can be made to emit electrons is by the application of an intense electric field, and the detailed understanding of the process is of comparatively recent date, because the first experiments in this connexion were concerned chiefly with the factors affecting the passage of a spark between two metal electrodes in various gases, with the result that the observations were greatly complicated by secondary effects due to the presence of the gaseous atmosphere. It is only in quite recent years that systematic experiments have been carried out in high vacua, and that the process has been examined in its simplest form.

The principal investigations are due to Millikan and his collaborators^{1,2,3} in America, B. S. Gossling⁴ in England, and to Rother⁵ in Germany. Millikan and Eyring² examined the electron emission from wires of tungsten suspended under slight tension in the axis of a copper cylinder, the dimensions of the apparatus being such that the field strength at the surface of the wire was 228 times the potential difference between the electrodes, the small radius of the wire (0.0012 cm.) causing a

large field intensity at the surface, the radius of the copper cylinder being 0.812 cm. Under these conditions electron emission became noticeable at potential gradients of the order 10^5 to 10^6 volts/cm., and Millikan defined as the critical gradient that potential gradient necessary to produce an emission, current or field current, of 9.7×10^{-12} amperes.

In this work it was shown that if a filament were used for the first time, the extraction of electrons by a sufficiently high field caused a change in the surface which made subsequent electron emission more difficult, so that if the field were for the first time increased to a maximum, and then decreased, the curves connecting the field currents with the potential difference were not superposed, the emission being less for the decreasing series. But once the specimen had been aged or conditioned in this way, the process became almost completely reversible, provided that the maximum current in the first series was not exceeded. If, at some later stage, the emission current were raised above that used for the first 'conditioning', the specimen again underwent a permanent change, reducing the emission for a given potential gradient, but the process once more became reversible provided that the second maximum was not exceeded. These changes were explained by the direct observation that the emission did not proceed uniformly from the whole surface of the wire, but was concentrated at a comparatively few minute spots, which presumably corresponded to surface irregularities, or chemical impurities. The conditioning of the surface was regarded as caused by the rounding-off of these minute irregularities by the positive ion bombardment due to the traces of gas remaining in the apparatus.

In the same way the emission was affected by the heat treatment of the specimen, general heat treatment at the lower temperatures lowering the critical gradient and increasing the emission owing to the expulsion of contaminating gases. On the other hand, prolonged heat treatment at very high temperatures increased the critical gradient considerably, owing presumably to the rounding-off of the surface peaks.

Once, however, a wire had reached a steady condition it became possible to measure the effect of temperature and applied potential upon the emission process, and the results obtained were of the greatest interest. In the first place it was found that the critical gradients and emission currents were completely independent of temperature over the range 300° – 1000° Abs.,

i.e. from room temperatures up to about 700°C. , but at higher temperatures the emission was no longer constant, and the two processes of thermionic emission and electron extraction took place together. From this point of view, therefore, the process resembles that of photo-electric emission in that it is independent of temperature over a very considerable range.

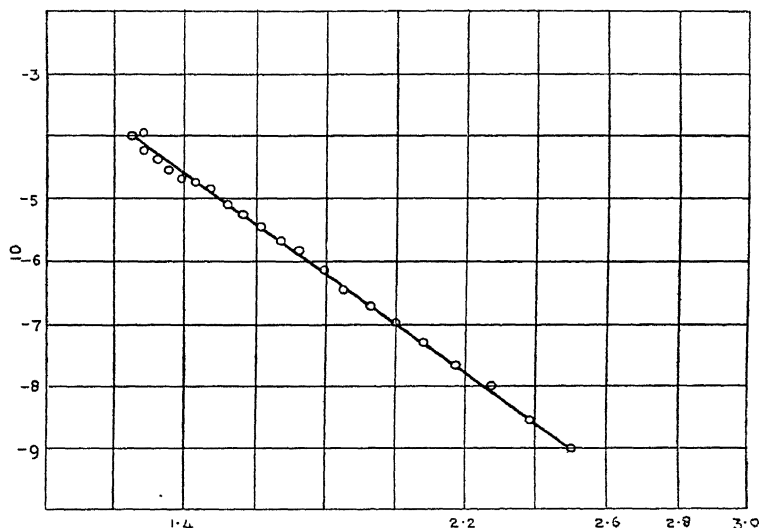


FIG. 44. Showing the relation between the Strong Field Emission current I and the applied potential V in the case of Tungsten. In the graph $\log I$ is plotted against $\frac{1}{V}$. In any given apparatus V is directly proportional to the Field strength F .

In a second paper Millikan and Lauritsen³ repeated and confirmed some of the earlier observations, and showed that a simple relation existed between the strength of the emission currents (I) and the field strength (F), the latter, for a given geometrical arrangement of the apparatus, being directly proportional to the potential gradient V . This relation is of the form

$$I = Ce^{-\frac{a}{F}}$$

so that if $\log I$ be plotted against $\frac{1}{F}$ a straight line is obtained, and Fig. 44 shows how remarkably well the experimental results

agree with a relation of this type. The same general conclusions were reached by B. S. Gossling,⁴ who also investigated the emission from tungsten, and confirmed the almost complete temperature-independence of the phenomenon. The experiments of Rother⁵ were carried out with very small distances between the two electrodes, but it was again shown that, except at the very smallest distances, the critical potential gradients were approximately constant when once the electrode had been rendered homogeneous, and completely freed from gases. These experiments also indicated that, after a thorough and drastic heat treatment in a high vacuum, a field strength as large as 10^7 volts/cm. was necessary in order to produce a noticeable emission, in agreement with the conclusion of Millikan that the emission takes place from irregularities which may become smoothed down by severe heat treatment.

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5. The Relations between the Emission Phenomena

In the preceding sections we have considered the emission phenomena as due to three separate processes, but from many points of view they are to be regarded as of a similar nature, since they are all concerned with the ease with which an electron can escape through the surface of the metal. We have already indicated that in the Einstein equation for the maximum velocity of the emitted electrons

$$Ve = \frac{1}{2}mv^2 = h\nu - h\nu_0 \quad . \quad . \quad . \quad . \quad (1)$$

the term $h\nu_0$ represented the least energy which had to be given to the electrons in order that they might break through the surface of the metal, whilst in the equations for thermionic emission

$$I = Ae^{-\frac{b}{\theta}} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and

$$I = C\theta^2 e^{-\frac{d}{\theta}} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

the terms b and d were, according to the simple theory, connected with the work done by an electron in crossing the surface, and

were in fact equal to $\frac{\phi}{k}$ where ϕ is this work. Consequently it is a matter of great importance to see whether these two quantities, the photo-electric and thermionic work functions, are the same for identical specimens, and much work has been done in this connexion. Since equation (3) is now generally preferred to equation (2), we shall consider this case only. In the case of the alkali metals the relations between the photo-electric and thermionic emissions were investigated by Richardson and Young,^{1,2} but their results were inconclusive owing to the presence of multiple threshold frequencies, and to the reactive nature of the metals, whilst for platinum, inconclusive results were obtained by Harrison,³ whose observations varied greatly with the exact heat treatment. It has, however, lately been shown by DuBridge⁴ that, when the last traces of gases are removed from platinum, the metal reaches a steady state in which the threshold frequency is 1962 A° , corresponding to a photo-electric work function of 6.30 volts, whilst the thermionic work function of equation (3) reaches a final value of 6.27 ± 0.07 volts, so that the two quantities agree within the limits of experimental accuracy. In the case of tungsten a similar conclusion has been reached by Warner,⁵ so that the identity of two functions appears to be established for pure metals *in vacuo*, although in the presence of gases it is certain that the two work functions are different.

In view of the great difficulty in obtaining reproducible results characteristic of pure metals, and free from all secondary effects, the absolute values of the various emission constants are seldom of much value in connexion with the problem of the ultimate structure of metals, but the independence of temperature shown by the photo-electric and intense field emission is a fact of the greatest importance, for it indicates that the 'free' electrons existing inside a metal are in such a condition that at ordinary temperatures their energies are almost independent of temperature. It is this fact, and the existence of a sharp photo-electric threshold, which form the chief characteristics of the emission processes from the point of view of metallic structure.

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VIII

THE CONTACT ELECTRICITY OF METALS

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1. General

THE phenomenon of contact electricity in metals, and the so-called Volta potential differences, occupy a very curious position in science. The fundamental discovery was made by Volta in 1801, at almost the same time as the much more famous discovery of the Voltaic cell. But at the end of the last century, and for some years afterwards, it was considered by many scientists that the Volta potential differences were due almost entirely to chemical reactions at the surfaces of metals, owing to the presence of moisture, gases, &c., and that if any real contact potential differences did exist between pure metals *in vacuo*, they were of very small magnitude. Recently it has been proved quite conclusively that real contact potentials do exist, so that the original view of Volta has been re-established.

On the theoretical side great confusion has existed as to the relations between contact potentials, thermo-electric properties, and electrolytic solution pressures, and as these relations can be discussed in terms of thermo-dynamics and general statistics we shall deal with these in the present chapter.

2. The Volta Potential Difference

The fundamental fact of contact electricity is that when two metals are placed in contact, electricity flows from one to the other. Thus when zinc is placed in contact with copper, the zinc acquires a positive and the copper a negative charge, showing that electrons have flowed from the zinc to the copper. This simple fact may be shown by taking zinc and copper plates with insulating handles, and connecting two plates with the opposite ter-

minals of a quadrant electrometer, when deflections are observed if the plates be brought into contact, and then moved apart. Experiments of this kind, together with repetitions of some of the original experiments of Volta are described by Lord Kelvin in a very interesting paper in the *Philosophical Magazine*.¹ The original simple methods of measuring the contact potential differences between pairs of metals have been considerably modified, and in general null methods are used in which the contact potential difference is balanced by an opposing electromotive force. In the so-called 'ionization methods', the air surrounding the specimens is ionized by some method, such as the introduction of a radium salt,² and when the exact balance is obtained no current flows across the space between one metal and the other, or alternatively no deflection is produced as the distance between the plates is varied. In order to measure the true contact potentials, it is, however, necessary to prepare the surfaces *in vacuo*, and apparatus for this purpose has been designed by Millikan and his collaborators.³

In this way it is possible to arrange the metals in a series, the so-called Volta series, so that if any two metals be connected together, a positive charge is acquired by the one which is the higher of the two in the series. These Volta potential differences are of the order 1 volt, and the values are additive quantities, so that the potential difference between two metals *A* and *Z* is the algebraic sum of those between *A* and *B*, *B* and *C* . . . *Y* and *Z*. This condition is really a thermo-dynamic necessity, since otherwise it would be possible to produce a continuous current in a closed circuit of several metals with no chemical or other changes to provide the necessary energy.

Unfortunately, as in the case of the emission constants, our exact knowledge of the Volta potential differences is extremely unreliable, for nearly all the measurements have been made in air, or else with specimens which were cleaned or polished in air, and subsequently placed in evacuated vessels. It has, of course, long been known that reactive metals such as those of the alkali group are at once oxidized by exposure to air, but it is only since the comparatively recent study of atmospheric corrosion that it has been recognized that nearly all metals acquire a thin oxide film almost instantaneously on exposure to the atmosphere. It may be argued that the presence of an oxide film at the surface of contact of two metals will produce no change in the contact potentials provided that a true metallic

connexion is made to the measuring instrument. For in this case we may imagine that the simple pair of metals, say copper and zinc, is replaced by the more complex series copper—copper oxide—zinc oxide—zinc, the contact potential of which will be the same as that of the combination copper—zinc. But it seems doubtful whether this conclusion is justified when we deal with oxide films, since the ‘contact’ of these with the underlying metal is no longer of a simple physical nature. In actual practice the contact potentials vary considerably with the conditions of preparation, gas pressure, &c., and much of the experimental work is rendered confusing by the fact that when factors such as heating in high vacuum have been investigated, the treatment has been applied to both metals, so that it has been impossible to see in which way the change took place. In some recent work, Dubois⁴ has measured the contact potential between a standard copper wire, which was left untreated throughout the experiments, and a series of metals both in the ordinary condition, and after a thorough outgassing in a high vacuum. In this way one metal only was submitted to the heat treatment, and the other remained unchanged, and in all cases the heating in a vacuum caused the metal to become more electro-negative, by amounts which sometimes exceeded half a volt, whilst heating at lower temperatures produced more complex results. It is clear therefore that the actual figures for the contact potentials are of little critical value, except in experiments such as those of Millikan³ in which the surface was prepared in a high vacuum, and even here the method suffers from the fact that the specimens were not annealed after the cutting, so that they were in a strained condition. In all cases an alkali metal is electro-positive to the alkaline earth metal which follows it in the Periodic Table, but in the B group the reverse is the case, and the Group 2 elements zinc, cadmium, and mercury are positive compared to the preceding metals copper, silver, and gold respectively. The differences between the behaviour of the A and B groups is thus similar to that met with in the case of the photo-electric threshold frequencies, melting-points, and lattice constants, and as we shall show in the general discussion the reason for this may be that zinc, cadmium, and mercury are only singly ionized in the solid state. But, apart from broad generalizations of this kind, a detailed comparison of contact potentials does not appear to be justified, whilst little or no systematic examination appears to have been made as to the effects of the

compositions of alloys upon their contact potentials. There is thus much scope for further work in this subject, but it may be emphasized that the only conditions under which the results will be satisfactory are those in which the metallic surface is prepared in a vacuum, and is then annealed to remove the effects of straining. In the case of alloys it is, of course, essential for these to be annealed or otherwise treated so that the specimen is in true equilibrium, and it should be realized that the science of Metallography has now progressed sufficiently for there to be no excuse for the omission of precautions of this kind.

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3. The Relations between Contact Potentials and the Photo-electric Effect

In the chapter on emission phenomena we have already indicated that, in order to obtain the true potential corresponding to the velocity of the emitted electrons, it is necessary to displace the measured potential difference between the electrodes by an amount equal to the contact potential between the metals of which the electrodes are composed. We may now consider these relations in greater detail, using the line of approach adopted by Millikan,¹ Richardson,² and Compton.³

According to the Einstein equation (p. 130) the velocity of the emitted photo-electrons may be written in the form

$$\frac{1}{2} mv^2 = h\nu - P = h\nu - h\nu_0 \quad . \quad . \quad . \quad (1)$$

where P represents the energy required to detach an electron from the metal, and ν_0 is the threshold frequency. We may now suppose that we have a metal A , and that we measure the stopping potential V_A required in order just to prevent the electrons emitted from the metal A under the influence of light of frequency ν from reaching the surrounding electrode or Faraday cylinder. Under these conditions the energy with which the electron is emitted ($h\nu - h\nu_0$) must just equal the potential V_A

plus the contact difference of potential (K_A) between the electrode and the Faraday cylinder,* so that

$$(V_A + K_A) e = h\nu - h\nu_{0A} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If we now make a similar experiment with a second metal B , but with light of the same frequency, we obtain an exactly similar relation

$$(V_B + K_B) e = h\nu - h\nu_{0B} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Hence the contact potential between A and B will be given by

$$(K_A - K_B) = \frac{h}{e}(\nu_{0B} - \nu_{0A}) - (V_B - V_A) \quad . \quad . \quad . \quad (4)$$

This equation was tested in great detail by Millikan, who found that it was always confirmed. In his first experiments, however, Millikan found that the term $(V_B - V_A)$ often had a definite value which might be as much as a volt, although in other cases the V terms for different metals were identical, so that the $(V_B - V_A)$ terms became zero. In a later paper⁴ it was shown that these effects were the result of spurious electro-motive forces which were regarded as due to the entanglement of electrons in the copper-oxide surface of the Faraday cylinder, and that, when these were done away with, the Contact Potentials and threshold frequencies were connected by the simple relation

$$K \quad K \quad - \quad \frac{h\nu_{0B} - h\nu_{0A}}{e} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

This conclusion was in agreement with the work of Kadesch and Hennings,⁵ and Page,⁶ and at present this equation probably gives the most reliable method of estimating true contact potentials between pure metals, since more photo-electric measurements have been made in high vacua than direct determinations of contact potentials.

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* We are here ignoring small energy changes such as those of the Peltier effect.

4. The Effect of Temperature upon Contact Potentials

The relations between temperature and contact potential are at present little understood, and the whole subject is in a very confused state. We have already seen that the contact potentials are to a first approximation connected with the photo-electric constants, by means of the relation (5),

$$K_A - K_B = \frac{h}{e}(\nu_{0B} - \nu_{0A}).$$

Strictly speaking this relation requires correction by a term to allow for the thermo-electric effects (Peltier Heat). In the very accurate work of Millikan and his collaborators, in which the metallic surfaces were prepared in a high vacuum, it was shown that all the ν_0 terms were independent of temperature, and consequently the contact potentials should be independent of temperature except for a small variation on account of the thermo-electric effects. As pointed out by Compton,¹ the differences to be expected on these grounds are of the order 10^{-4} to 10^{-5} volts per degree Centigrade, and are thus very small.

Apart from the work of Millikan, however, all the experimental investigations indicate a very much greater temperature variation of contact potential, of the order 10^{-2} to 10^{-3} volts per degree Centigrade, the chief investigations in this connexion being due to Compton,¹ Erskine-Murray,² Burbidge,³ Anderson,⁴ and McHenry.⁵ Unfortunately all these experiments were either carried out in air, or else with specimens cleaned in air, and subsequently placed in evacuated vessels, and all of them are thus open to criticism. It has been shown by Bidwell⁶ that many of the metallic oxides possess very high thermo-electric powers, values as high as 1 milli-volt per degree having been found in some cases, and it was suggested by Compton that this may be the cause of the abnormally high values found experimentally for the temperature variation of contact potential differences between metal surfaces prepared in air.

It has been shown by Ives⁷ that for the alkali-metals a slight shift in the threshold frequency ν_0 does occur at the temperature of liquid air, this being accompanied by a corresponding change in contact potential. In this work the potassium film was prepared by distillation *in vacuo*, in contrast to the method of Millikan in which a fresh surface was cut in a vacuum. It does not, however, seem likely that this explanation will account for the apparent discrepancy between the conclusions of Millikan and

the results of the investigators referred to above, since most of the change found by Ives occurred below 0°C. , and there is thus much need for further investigation of the effect of temperature upon contact potentials between metal surfaces prepared in a high vacuum.

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5. The Relations between the Contact Potentials and Thermo-Electric Potentials

For a long time great confusion has arisen in connexion with the relations between the contact potentials and the thermo-electric properties, and it may be well therefore to deal with this point in some detail. We may note at the outset that we cannot really compare contact electromotive force directly with the electromotive force of a thermo-couple. For, as was pointed out by Lord Kelvin,¹ contact potential differences occur between pairs of metals at a constant temperature, whilst thermo-electromotive forces depend essentially on differences in temperature. If therefore we wish to make a comparison, it must be between the thermo-electromotive forces and the *temperature variation* of contact potentials.

The second point over which confusion has arisen is in connexion with the smallness of the Peltier Heat change, for it has been frequently argued that if contact potentials of the order one volt do really exist at the junction between two metals, there should be a large heat evolution or absorption when a current crosses the boundary, and, conversely, since the actual heat change is very small, it has been argued that the real contact potentials are of the order milli-volts, and hence that the large Volta potential differences must be due to secondary effects. This point of view was at one time vigorously supported by Sir Oliver Lodge, and if it is examined critically it will be seen that it really involves the assumption that, when a current crosses the boundary, all the work done against the potential difference will appear as a reversible heat evolution or absorption.

But in reality this is by no means necessary, and most of the work may be stored up as electrostatic energy. This may be shown by the following method, which is due to Lord Kelvin.

Suppose we have two metals *X* and *Y*, of which *X* is electro-positive to *Y* so that electrons flow from *X* to *Y* when the two metals are connected at the junction *J*. Let *CD* be a piece of the metal *Y* resting without friction on the surface of *EF* in the position shown. Then on account of the opposite electrifications of the two surfaces *AB* and *CD*, the plate *CD* will be subject to a pull inwards, and if by means of an external force we draw *CD* out, a current will flow from *AB* through the metal *X* across

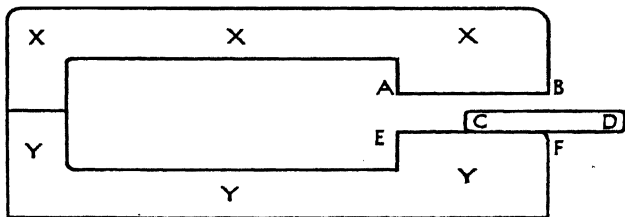


FIG. 45.

the junction *J*, and electrons will flow in the opposite direction. As the current of electricity crosses *J*, it will give rise to the Peltier Heat Effect, and since everything is here at constant temperature we can legitimately apply a simple thermodynamic cycle. When, therefore, the plate *CD* is drawn out there is a production (or absorption) of heat due to the Peltier Effect at *J*. Apart from this there is also the possibility that there may be 'quasi-Peltier Effects' at the air-or-ether-metal surfaces between *AB* and *EF*, 'produced by the electricity crossing the border between air or ether at the surface of either metal, and the homogeneous metal inside'. The magnitude of these effects, which may or may not exist, is unknown, and we may denote by *Q* the total heat produced as the result of the Peltier Effect at *J*, and the quasi-Peltier Effects at the surfaces. The thermodynamic cycle then consists of the following processes:

1. The whole apparatus is imagined to be coated with a varnish or similar covering which is impervious to heat, and *CD* is drawn out very slowly so that the process is adiabatic, and the temperature of the whole gradually rises from θ_1 to θ_2 . In order to do this a certain amount of work will have to be done by the external force.

2. The whole apparatus is placed in a thermostat at constant temperature θ_2 , and CD is allowed to move inwards very slowly until a certain quantity of heat H is taken in by the apparatus from the thermostat. This process is an isothermal one at θ_2 .
3. The plate CD is then allowed to move inwards adiabatically; being again imagined coated with impermeable varnish, until the temperature sinks from θ_2 to θ_1 .
4. Finally the plate is drawn out isothermally at θ_1 until it reaches its original position, and in doing this a quantity of heat H^1 will have to be removed in order to prevent the temperature rising.

These four operations constitute a complete cycle of operations, and since at any instant the whole apparatus is at the same temperature, a Carnot cycle can be applied, and the result obtained in this way is:

$$\frac{dV}{d\theta} = \frac{Q}{\theta}$$

where V is the contact potential difference at the junction. Consequently when the plate CD is drawn out, the heat produced at J is not the thermal equivalent of the drawing out of the copper plate, most of this work being used in storing up electrostatic energy, and only a small part being spent on the heat produced at J , or, more properly, as the difference between the Peltier Effect at J , and the quasi-Peltier Heat Effects (if any), in the surface layers at AB and EF when they undergo changes of electrification.

The idea that the Peltier Heat produced when a current crosses a metallic junction is the thermal equivalent of the work done is thus quite incorrect, although this supposed equality has frequently appeared in the theoretical development of the subject.

The method adopted by Lord Kelvin leads to the relation above, but it cannot be extended because the behaviour of a single junction cannot be further investigated thermodynamically without introducing a return path. The subject has, however, been investigated statistically by J. A. V. Butler,² who obtains the following relation for the contact potential E between two metals A and B ,

where $U = (h\nu_{0A} - h\nu_{0B})$ F is the total energy change in the passage of the electrons from one metal to the other, F is

one Faraday, and K is a constant depending on the statistical conditions. This line of approach really involves assumptions concerning the way in which equilibrium is attained between an electron atmosphere and a metal, but the equation is introduced here because it is required in order to understand the relations between contact potentials and electrode potentials which are discussed in the next section.

REFERENCES

1. Lord Kelvin. *Phil. Mag.* 1898, 46, 82.
2. Butler. *Phil. Mag.* 1924, 48, 746.

6. The Relations between Contact Potentials and Electrolytic Solution Potentials

As stated in the Preface, we do not propose to deal here with the electro-chemical properties of metals, but as confusion has existed in connexion with the relations between contact potentials and electrode potentials, it may be well to discuss this question in some detail, since this problem has recently been solved satisfactorily by J. A. V. Butler.^{1, 2, 3}

It has long been known that when two metals are placed in an electrolyte, and then joined by a wire, a galvanic cell is formed, and a current flows through the wire, but the exact source of the electromotive force is by no means so clear. According to the older views of Nernst, the seat of the electromotive force was to be found at the electrodes, and each electrode was regarded as emitting positive ions, until a state of equilibrium was reached in which the tendency to emit ions was balanced by the electric charge left on the electrode plus the pressure of the ions in the solution. According to this point of view, each metal in a normal solution of one of its salts had a characteristic solution potential, and the electromotive force of a galvanic cell, free from secondary effects, was the difference of the potentials of the two electrodes. This explanation of the process was supported by the discovery in the Gibbs-Helmholtz equation, that the electrical energy generated in the galvanic cell was equal to that of the chemical process which took place, and as long as it was thought that the true contact potentials in the part of the circuit outside the electrolyte were only of the order of a few milli-volts, corresponding to the Peltier Effect, the whole conception appeared to be satisfactory. But with the discovery by Millikan and by Richardson that real contact poten-

tials of the order one volt existed between pure metals *in vacuo*, difficulties were at once apparent, and we may now consider the following explanation, given by Butler.

We may consider a simple cell in which the electrodes are of zinc and copper, the two electrodes being joined outside the cell by means of copper wire. The reaction which takes place may then be considered as divided into three parts:

1. The solution of zinc at the one electrode.
2. The deposition of copper from solution on to the copper electrode.
3. The passage of electrons from zinc to copper.

It was then shown by Butler that if we accept the contact potential differences deduced from the photo-electric work functions, the energy change corresponding to the third process is large, and in fact accounts for a considerable fraction, which is often the greater part of the total energy of the chemical reaction taking place in the cell. Thus with copper and zinc, the contact potential difference deduced from the photo-electric work function is 0.6 volts, and the difference between the heats of solution expressed in volts is 1.15 volts, whilst the measured *E.M.F.* of the cell is 1.10 volts.

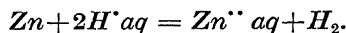
It was further shown by Butler that a general correspondence existed between the contact potentials of the different metals against platinum, and the corresponding normal electrolytic solution potentials against the normal hydrogen electrode, in which the electrode material is platinum, and the metal junction is that between metal and platinum. The following examples, which are taken from Butler's paper, may make this point clear.

TABLE XXIX

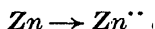
<i>Metal.</i>	<i>Potential Contact Difference against Pt.</i>	<i>Electrolytic Normal Potential against H.-Pt. Electrode.</i>
K.	2.95	2.92
Na.	2.6	2.71
Li.	2.1	2.96
Ca.	1.8	2.5
Mg.	1.7	1.49
Al.	1.4	1.34
Zn.	1.0	0.76
Cd.	0.90	0.40
Sn.	0.6	0.14
Cu.	0.4	-0.36

The conclusion which is drawn from this rough correspondence is that the contact potential difference is mainly responsible for the E.M.F. of the cell, and that the older conception, that almost all of the E.M.F. is situated at the contact between the electrodes and the solution, is incorrect.

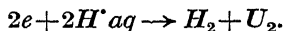
It remains, however, to be shown that this conclusion is not in conflict with the Gibbs-Helmholtz equation, and this may be done as follows by considering a simple (*Zn-Pt*) cell in which zinc dissolves and hydrogen is liberated, so that the total reaction is



At the metal electrode, the process is simply the passage of the metal ions from the metal into solution, and we may unite the total energy change* of this as U_1



At the platinum electrode, where hydrogen is discharged, we may write:



Whilst at the junction between the metals the energy change on account of the contact potential difference may be written:

$$2e_{\text{Zn} \rightarrow \text{Pt}} = U_3 = (h\nu_{0\text{Zn}} - h\nu_{0\text{Pt}}) F.$$

In this equation we again ignore the small thermo-electric effects. The sum of the total energy changes throughout the cell, provided no external electrical work is done, will then be equal to the heat of reaction, so that

$$U = -Q = U_1 + (h\nu_{0\text{Zn}} - h\nu_{0\text{Pt}}) F + U_2 \quad . \quad . \quad . \quad (1)$$

In this way, if we know the heat of reaction Q , and the threshold frequencies, we can determine the sum of the energy changes at the two electrodes ($U_1 + U_2$). Owing to the uncertainty of the threshold frequencies, however, Butler also obtained values for the energy changes at the electrodes by an alternative method which served as a rough check upon the values obtained from equation (1). For this purpose the metal is imagined to be vaporized (heat absorbed S), and the vapour ionized (heat of ionization J). The ionized electrons are then returned to the metal (heat evolved ϕF where ϕ is the thermionic work function), and the metal ions dissolved in water (heat of hydration H).

* By the total energy change at a junction is meant the heat effect when no electrical work is done. In the galvanic cell only a small part of the energy of the reaction is liberated as heat.

The total energy change corresponding to the passage of metal ions into solution is then

$$Q_1 = H + \phi F - J - S \quad . \quad . \quad . \quad . \quad (2)$$

All these terms are known roughly for some metals, and in this way equation (2) forms a check on the values determined from equation (1), although the values are too approximate to have any precise meaning. The conclusion drawn is that the energy change taking place at the electrode is small compared with the total energy change in the cell, and is roughly of the same order as that occurring in the solution of salts, so that qualitatively there is no conflict between the Gibbs-Helmholtz equation and the view that the contact potential difference is the main seat of the electromotive force of a galvanic cell.

Finally, Butler was able to show quantitatively that the Gibbs-Helmholtz equation followed directly from the above conceptions, and this may be done in the following way, if we imagine a simple cell in which the chemical reaction is, for example, represented by the equation:

In this case at the zinc electrode, the process taking place is the solution of zinc, and at the copper electrode, the process is the deposition of copper, whilst at the metal-metal junction the electrons do work against the contact potential difference. At the zinc electrode, therefore, the condition for equilibrium is given by the relation:

$$f_{Zn^{++}(\text{Metal})} = f_{Zn^{++}(\text{Solution})} + 2E_1 F,$$

where $f_{(\text{Metal})}$ and $f_{(\text{Solution})}$ are the partial free energies of the zinc ions in the metal and the solution respectively.

At the copper electrode the corresponding relation is

$$f_{Cu^{++}(\text{Metal})} = f_{Cu^{++}(\text{Solution})} + 2E_2 F,$$

Whilst at the metal-metal junction, we have

where $f_{e(Zn)}$ and $f_{e(Cu)}$ are the partial free energies of the electrons in the two metals.

Considering the change, we have for the free energy changes:

1. In the solution of zinc $\Delta f_1 = f_{Zn^{++}(\text{Solution})} - f_{Zn^{++}(\text{Metal})}$.
2. In the deposition of copper $\Delta f_2 = f_{Cu^{++}(\text{Metal})} - f_{Cu^{++}(\text{Solution})}$.

3. In the passage of 2 equivalents of electrons from zinc to copper $\Delta f_3 = 2(f_{\epsilon(Cu)} - f_{\epsilon(Zn)})$.

So that the total free energy change Δf is given by

$$\begin{aligned}\Delta f &= \Delta f_1 + \Delta f_2 + \Delta f_3 \\ &= (2E_2 - 2E_1 - 2E_{Zn \rightarrow Cu})F \\ &= 2EF\end{aligned}$$

where E is the electromotive force of the whole cell.

The free energy change of the reaction is therefore equal to the electromotive work, and all the thermodynamic relations, including the Gibbs-Helmholtz equation, can be applied. In this way the older rival 'contact' and 'chemical' theories of the source of the electromotive force are satisfactorily reconciled, each representing one aspect of the truth. It follows from this explanation that attempts to determine absolute potential differences at electrodes must take into account the possibility of contact potential differences between the standard and the experimental electrode metals. On the other hand the E.M.F. of a cell involving a reversible oxidation process at an inert electrode is not affected by the electrode material, because, if the effect of the metal-metal junction is considered, any variation in the electrode material will affect the potential differences at its ends by equal amounts.

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1. Butler. *Phil. Mag.* 1924, 48, 927.
2. Butler. *Trans. Faraday Soc.* 1924, 19, 729.
3. Butler. *Trans. Faraday Soc.* 1924, 19, 734.

SECTION II

INTRODUCTORY NOTE

IN attempting any description of the various electronic theories of metals, the first difficulty encountered is the widely different points of view from which such theories are of interest. For while the greater part of the theoretical work has been confined to the electrical and thermal properties, the conclusions naturally bear indirectly upon other characteristics, and the complete theory must, of course, eventually embrace the whole of the properties of the metallic state. There are thus many readers to whom a general survey of theoretical work is of interest, but who do not wish to study the details of the mathematical treatment. The second difficulty is that, although a great deal of the older work has now been revised or discarded, the more recent theories involve so much of what is really mathematical technique, that it is from many points of view much more easy to approach the subject by considering first the earlier theories, than to plunge directly into the strange conceptions which are resulting from the new quantum mechanics.

In the hope of meeting these difficulties, and of making the book appeal to as wide a range of readers as possible, the following policy has been adopted. Except for some of the shorter intermediate theories which are dealt with in Chapter XI, each of the main theories is treated in a separate chapter, which begins with a general description, written, so far as is possible, in non-mathematical form. These general accounts are then followed by more detailed descriptions, leading to the derivation of the various equations for the electrical conductivity and other constants. Each chapter then concludes with a critical discussion of the theory concerned, and this is intended for both the general reader, and the more serious student. In this way it is hoped that, by reading the general descriptions and discussions, the reader will be able to obtain a survey of the main trend of the theoretical work, whilst those who wish to study the subject more thoroughly will find the details which they require. This policy naturally involves a little repetition in some places, but it seemed to offer the best solution of the difficulties referred to.

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1. Introductory

THE free electron, or electron-gas theory, was the first to give a comprehensive account of the electrical and thermal properties of metals supported by anything in the way of quantitative evidence. It was the result, on the one hand, of the discovery of the electron as a definite constituent of matter, and on the other hand of the striking success of the kinetic theory of gases in so many directions. The theory was first put forward by Drude¹ in 1900, and has since been extended by many workers. It is, however, probably better to separate the original simple theory from the more complicated developments, for these have, in general, only been concerned with minor details, and with the removal of the admittedly crude simplifications made in the original theory. The majority of these simplifications were frankly recognized as such by Drude, whose work was intended as a preliminary survey of the whole field of the electrical, thermal, and optical properties of metals. The theory is no longer generally accepted, but as a first attempt its success was most striking, and particularly so in view of the very simple assumptions which were made.

REFERENCE

1. Drude. *Ann. d. Physik*, 1900, **1**, 566, **3**, 369.

2. General

The general picture presented by the Drude theory is quite simple. The metals are supposed to contain a number of free electrons moving in the spaces between the atoms, and it is assumed that the motion of these electrons can be treated as though they were molecules of an ideal gas as pictured by the kinetic theory. When no current is flowing through the metal

the electrons are considered to move quite at random, colliding sometimes with each other and, much more frequently, with the atoms, so that on the whole there is no resultant flow in any one direction. But when an electric force is applied, it causes a general drift of the electrons in one direction, and in this way the current is carried.

On this theory, therefore, the electrical conductivity depends on the number of free electrons per unit volume of the metal, their velocity, and the way in which their collisions with the atoms interfere with the general drift of the electrons in the direction of the electric force. Since the radius of an electron is of the order 10^{-13} cm., whilst that* of an atom is 10^{-8} cm., the number of collisions of electrons with one another is assumed to be negligible compared with the number of collisions between atoms and electrons. For the chance of a collision depends on the square of the dimensions, and hence, unless the electrons are very much more numerous than the atoms, the chance of a given electron hitting an atom is about 10^{10} times its chance of hitting another electron.

The electron-gas theory then makes the simple assumption that the kinetic energy of the electrons, in the absence of an electric force is that of a gas molecule at the same temperature, and hence, since the mass of an electron is known, the velocities of the electrons at a given temperature can be calculated from the kinetic theory. For all ordinary currents the general drift produced by the electric force is small compared with their normal gas velocity.

In the same way, when one end of a metal is heated, the electrons tend to flow from the hotter to the colder parts, just as the hotter molecules of an unequally heated volume of gas tend to diffuse into the colder parts. The comparison is, of course, with the true *conductivity* of a gas, and not with the equalization of heat by convection. From this point of view, the high thermal conductivity of metals is due to the small mass, and consequent high velocity of the electrons, since the true thermal conductivity of a gas varies directly as the velocity of its molecules.

* We are here assuming, as in the earlier theories, that the effective radius of an atom for the collision process is of the same order as the interatomic distance in the solid metal. This is not really the case, as is shown by the Ramsauer effect, but the general conclusion is not invalidated as long as we look upon the collisions as governed by what we may call the 'particle' properties of the electrons and atoms. The new wave theories indicate that this is only one aspect of the truth, but these conceptions lie quite outside the older work.

Further, since the theory regards the electric current as being carried by moving charges of electricity, we can at once understand how the motions of these particles are affected by the presence of magnetic fields, and a general understanding of the galvano-magnetic phenomena (the Hall Effect, &c.) becomes possible. It is not, however, so easy to see why these effects should have different signs in different metals, and this can in fact only be explained by making rather improbable secondary hypotheses as to the effect of the magnetic field upon the mechanism of the collisions between the electrons and the atoms.

The thermo-electric properties are accounted for on the assumption that, in an unequally heated metal, the electrons will in general tend to flow from the hotter to the colder part, and that in so doing they will cause a difference in potential to be set up so that equilibrium is eventually established when this potential difference just balances the differences in the pressure of the electron gas in the hot and cold parts. In this way we are led to expect a difference in potential to be set up in an unsymmetrically heated conductor (Benedick's Thermo-Electric Effect), and also transference of heat when a current flows down an unequally heated conductor (Thomson Effect). As we shall see later, it is not so clear why these effects should have different signs in different metals.

Similarly, when metals are placed in contact, the pressures of the electrons in the two metals are in general different, so that the electrons tend to flow from one metal to another until this tendency is balanced by the difference in potential set up. In this case the process is a little more complex owing to the fact that when an electron crosses the surface of a metal, it experiences an energy change, the so-called work of emission, which has to be taken into account. The development of this side of the theory was rather confused, owing to the frequent use of the argument, which we have already (p. 155) shown to be fallacious, that the whole of the work done by a current against a potential difference at the boundary between two metals should appear as heat. When this fallacy is avoided the expressions deduced for the contact potential between two metals involve the temperature, the work of emission, and the electron concentration in the two metals, whilst the expression for the Peltier Heat involves the electron concentrations and temperature only.

3. Derivations of the Equations for the Thermal and Electrical Conductivities

Drude originally considered the possibility of electric conduction in metals taking place on account of both positive and negative carriers, but so many facts have indicated that all the carriers are the negatively charged electrons, that we shall consider this conception alone. In attempting to deduce an expression for the electrical conductivity from this point of view, we have to make certain simplifying assumptions, of which the most important are as follows:

Owing to the small mass of the electrons, about $1/1840$ that of a hydrogen atom, their velocity must be very great if they behave as particles of an ideal gas, and calculations from the kinetic theory show that the velocity will be of the order 10^7 cm. per second. At normal current densities, the velocity of general drift of the electrons (u) caused by the electric force will therefore be very small compared with the normal gas velocity (v). Thus for copper at a current density of 10^4 amps. per sq. cm., u is about 1% of v , so that for the current densities with which we generally deal, we are justified in assuming that u will have little effect upon the length of the mean free path (λ) between two collisions, and we may unite $\lambda = vt$, where t is the time between two collisions.

We assume further that the effect of the electric field on the motion of an electron is completely destroyed by the collision, so that it rebounds with the normal velocity of thermal agitation (v). Strictly speaking this is not true, but the assumption is probably accurate to a sufficient degree in view of the fact that u is small compared with v , and that many other approximations are made.

Let us now suppose that an electric field X acts on the metal, and produces a general drift (u) of the electrons in the free paths between their collisions. It must be understood that this will be a general effect only. Some electrons will still move one way, and some another, but whereas in the absence of an electric force there is no resultant flow in any direction, the presence of an electric force will cause a general flow in its direction, and we may treat this statistically as though each electron acquired a uniform velocity u in the direction of the force.

If m is the mass of an electron, t the time between two col-

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lisions, and e the electronic charge, the mean velocity given to the electrons by the electric force will be

$$u = \frac{1}{2} X \frac{e}{m} t$$

because the force acts on the electrons for the average time t , at the end of which the added velocity is $X \frac{e}{m} t$, and since this is acquired steadily the mean velocity will be $\frac{1}{2} X \frac{e}{m} t$.

If there are n electrons per unit volume, the quantity of electricity carried in unit time across a unit area at right angles to the electric force is

$$i = neu = \frac{1}{2} \frac{nXe^2t}{m}.$$

Since u is small compared with v , we assume that λ is the same whether the current is flowing or not, in which case we may unite $t = \frac{\lambda}{v}$, and the specific electrical conductivity may be written:

$$C = \frac{i}{X} = \frac{ne^2\lambda}{2mv} = \frac{ne^2\lambda v}{2mv^2}.$$

Now $\frac{1}{2} mv^2$ is the kinetic energy of an electron, and by the fundamental assumption of the theory, this must be equal to the kinetic energy of a gas molecule at the same temperature, which is given by $a\theta$, where θ is the absolute temperature, and a is a fundamental constant of value 2.02×10^{-16} ergs per $^\circ\text{C}$.

The expression for the specific electrical conductivity thus reduces to

$$\frac{ne^2\lambda v}{4a\theta} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and this is the fundamental equation of the simple theory. It is sometimes written in the alternative form $C = \frac{ne^2\lambda v}{6R\theta}$; in this case we refer to the gram-molecule, and the kinetic energy of the gram-molecule is given by $\frac{3}{2}R\theta$, where R is the gas constant.

The expression for the thermal conductivity of a metal from the point of view of this simple theory is that for the thermal conductivity of the electrons considered as a gas at the same temperature. This is given directly by the Kinetic Theory as

$$. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where a is the constant previously referred to. The alternative form is $K = \frac{nv\lambda R}{2}$. The proof of this well-known equation is to be found in almost any text book on the kinetic theory of gases (e.g. Jeans, *Dynamical Theory of Gases*, 1921, p. 290), and is therefore not reproduced.

4. The Wiedemann-Franz Ratio

From the above equations for the thermal and electrical conductivities we may compare their ratio, which reduces to

$$\frac{K}{C} = \frac{\frac{nv\lambda a}{3}}{\frac{ne^2\lambda v}{4a\theta}}$$

This expression is independent of both n and λ , which are the quantities which vary from one metal to another, and hence the theory predicts a constant Wiedemann-Franz ratio in general agreement with fact.

Further, when we insert the numerical values in equation (3) we find that at 0°C. the theoretical value for the Wiedemann-Franz ratio is 6.3×10^{10} , which is remarkably near to the experimental value. This prediction of the approximate value of the Wiedemann-Franz ratio is the one great triumph of the simple electron gas theory, and must admittedly be regarded as most striking. Considering the very simple assumptions which the theory involves, it is, to say the least of it, remarkable, that two such apparently different constants as the thermal and electrical conductivities should have been accounted for so satisfactorily.

The theory also leads us to expect a very slight deviation from Ohm's Law at extremely high current densities, because in this case it is no longer justifiable to assume that the velocity of general drift (u) given to the electrons, is small compared with their normal gas velocity (v). Calculation shows that, unless the free paths are very large compared with the interatomic distances, the deviations from Ohm's Law to be expected at current densities of the order 10^6 amperes per sq. cm. are very much smaller than those which Bridgman claimed to have detected (p. 2). This was originally used as a strong argument against the simple electron-gas theory, but, as we have already seen (p. 2), the more detailed work of Barlow indicates that no detectable deviation exists, so that this criticism of the older

theory is no longer justified, and the theory is in agreement with the facts, since the deviation to be expected is within the limits of the experimental methods.

5. Contact Potentials and Thermo-Electric Properties

The simple electron gas theory is able to give a general account of the Contact Potentials and Thermo-Electric properties, although the theoretical equations lead to inconsistencies as regards the numbers of free electrons required. Since the pressures of the electrons are not necessarily the same in different metals, we shall in general expect electrons to flow from one metal to another if the two are placed in contact. In this way a potential difference will be created, and we may expect equilibrium to be attained when the number of electrons crossing the boundary in one direction in a given time, owing to the difference in pressure, is equal to the number crossing in the opposite direction, owing to the potential difference set up. The theoretical development of this conception was, however, very confused owing, firstly, to the fallacious argument (see p. 155) that all the work done by an electron in crossing the boundary must appear as heat, and, secondly, because, in some of the earlier developments of the theory, it was forgotten that when an electron crosses the surface of a metal, a definite amount of work has to be done. It is this force, corresponding to the work of emission, which keeps the electrons in the metal at ordinary temperatures.

The problem may be approached by the following method, which is due essentially to O. W. Richardson.¹ We may assume that the ordinary kinetic theory of equilibrium can be applied, so that in any system at a constant temperature θ , if n_1 and n_2 are the concentrations of electrons at any two points A and B , and if W is the work done in taking an electron from A to B , then at equilibrium

$$\frac{n_2}{n_1} = e^{-\frac{W}{R\theta}} \text{ (or } e^{-\frac{3W}{2a\theta}} \text{)} \quad (4)$$

where R (or a) are the previous gas constants.

We may consider now a piece of metal present in a small evacuated insulated space at a constant temperature θ . The metal will begin to emit negative electrons until a steady state is reached in which the positive charge acquired by the metal pulls back as many electrons in a given time as are emitted in the same period.

If at any external point, n and V are respectively the number of electrons per unit volume, and the potential, then, since there is equilibrium between the inside and the outside of the metal, we have

$$\frac{n}{n_1} = e^{-[w_1 + e(V - V_1)] \frac{3}{2a\theta}} \quad . \quad . \quad . \quad . \quad (5)$$

where w_1 is the work done by the electron in crossing the surface, and V_1 is the potential at the surface.

Now suppose that instead of one metal we have two different metals present in the same evacuated and insulated space, and let w_1 and V_1 , and w_2 and V_2 refer to the two metals respectively. Then an equilibrium will finally be set up in which each metal emits as many electrons as it gains in a given time.

Then if n_1 and n_2 are the numbers of electrons per unit volume in the two metals,

so that W , the work done in taking an electron from one metal to another will be given by

$$W = \frac{2}{3} a\theta \log \frac{n_2}{n_1}.$$

But W must also equal the work done in going through the surface of the one metal (w_1), across the intervening space to the second metal ($e(V_2 - V_1)$), and through the second surface (w_2). So that

$$W = \frac{2}{3} a\theta \log \frac{n_2}{n_1} = w_1 + e(V_2 - V_1) - w_2$$

giving

$$V_2 - V_1 = \frac{w_2 - w_1}{e} + \frac{2}{3} \frac{a}{e} \theta \log \frac{n_2}{n_1} \quad . \quad . \quad . \quad (6)$$

This equation refers to two metals separated from one another, but an argument of the kind used in deducing the Phase Rule shows that it also applies to the case of two metals in contact, so that equation (6) gives the true contact potential, which thus requires a knowledge of the w terms, the magnitudes of which are very much greater than the term $\frac{2}{3} \frac{a}{e} \theta \log \frac{n_2}{n_1}$, so that the Contact Potentials depend essentially on the w terms, which cannot be evaluated from the point of view of the simple gas theory.

Now the Peltier Effect is a measure of the heat liberated when a steady current passes across the junction of two metals, and,

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as we have already shown, the work done in taking an electron from one metal to another by crossing the outer surfaces is:

$$(w_1 - w_2) + e(V_2 - V_1)$$

which is equal to

$$\frac{2}{3} \frac{a}{e} \theta \log \frac{n_2}{n_1},$$

Consequently the work done per unit charge is given by

$$P = \frac{2}{3} a \theta \log \frac{n_2}{n_1}. \quad . \quad . \quad . \quad . \quad (7)$$

It can be shown that if the whole energy change in crossing the boundaries is given by the term $(w_1 - w_2)$, then the expression $\frac{2}{3} a \theta \log \frac{n_2}{n_1}$ represents the whole of the heating or cooling effect due to the passage of the current across the junction, no energy being changed into other forms. This is really only true if the conditions of motion of the electrons in the two metals are identical so that no transfer of kinetic energy takes place when the electron crosses the boundary when a steady current is flowing, but possible differences of this kind are neglected in the simple theory, so that equation (7) gives the Peltier Effect.

As we have already seen (Chapter VI), the magnitude of the Peltier Effect is very small, and even in the case of bismuth and antimony only amounts to 1/30 volts. In this case equation (7) shows that $\frac{n_2}{n_1} = 3.8$, and this indicates that the numbers of electrons per unit volume are approximately equal for all metals, since, although the Peltier Effect for bismuth and antimony is abnormally large, it only requires the one metal to have about four times as many electrons per unit volume as the other.

In the Thomson Effect we deal with the transference of heat by an electric current flowing through an unequally heated conductor. Since the pressure of the electrons in a metal depends upon the temperature, there must be corresponding differences in electromotive force in order to prevent all the electrons from drifting from one point to another. The expression for the Thomson coefficient may then be deduced by the following method which is again due to Richardson (*loc. cit.*). We imagine two specimens of the same metal A and A' kept at constant temperatures θ and θ' , and connected by a thin rod of the same metal covered with some insulating substance which prevents the evaporation of electrons. A and A' are surrounded by

evacuated chambers, and electrons can be transferred reversibly from one chamber to another by means of a suitable piston and cylinder arrangement. Since A and A' are at different temperatures there is a continual flow of heat down the narrow rod.

Under these conditions each piece of metal gives off electrons until an equilibrium is produced, and the potentials acquired may be written V and V' . These potentials are not necessarily the same, even though the two metals are connected by the thin rod. A difference of potential may, for example, arise if contact potentials vary with temperature, and we may therefore surround A by a potential filter maintained at the potential V' . Under these conditions no work against *electrical forces* will have

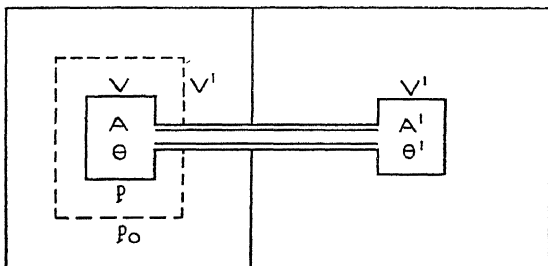


FIG. 46.

to be done if we remove an electron from that part of the chamber at θ which is outside the filter, to the chamber at θ' . The corresponding equilibrium pressures, which are proportional to the number of electrons per unit volume may be denoted by p terms for the vapour phase, and P terms for the electrons within the metal.

The cycle of operations now consists in evaporating N electrons from A through the potential filter, bringing them by reversible processes to the same temperature as those outside A' , condensing them into A' , and then allowing them to flow down the narrow conductor from θ' to θ . In this last process the heat absorbed will be $Ne \int_{\theta'}^{\theta} \sigma d\theta$, where σ is the Thomson Coefficient.

We assume, further, that the laws of thermodynamics can be applied to this cycle of operations in spite of the continuous flow of heat which takes place down the rod from A' to A . This is the same assumption involved in the Kelvin treatment of thermoelectricity, and we shall discuss its justification later (p. 202).

In evaporating from A , the work done is $NR\theta$, and the heat

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absorbed is $N(w + e(V' - V) + R\theta)$. The work during the adiabatic transformation from θ to θ' is $\frac{NR}{1-\gamma}(\theta - \theta')$ where γ is the ratio of the specific heats at constant pressure and constant volume; since the transformation is adiabatic the heat absorbed is zero, and the pressure changes from p_0 to $p_0 \left(\frac{\theta}{\theta'}\right)^{\gamma/(1-\gamma)}$. The electrons are then expanded isothermally to the pressure p' during which the work done equals $-NR\theta' \log \left(\frac{p'}{p_0}\right) \left(\frac{\theta}{\theta'}\right)^{\gamma/\gamma-1}$, and a corresponding amount of heat is absorbed. In condensing into A' at temperature θ' and pressure p' , the work is $-NR\theta'$ and the heat absorbed $-N(w' + R\theta')$. Finally, on flowing down the conductor from θ' to θ , the heat absorbed is $Ne \int_{\theta'}^{\theta} \sigma d\theta$. If we now apply the second law of thermodynamics to the above cycle we have $\int \frac{dQ}{\theta} = 0$, and hence

$$\frac{NR\theta' \log \left(\frac{p'}{p_0}\right) \left(\frac{\theta}{\theta'}\right)^{\gamma/\gamma-1}}{\theta} - \frac{NR\theta' \log \left(\frac{p'}{p_0}\right) \left(\frac{\theta}{\theta'}\right)}{\theta'} - \frac{-N(w' + R\theta')}{\theta'} + Ne \int_{\theta'}^{\theta} \frac{\sigma}{\theta} d\theta = 0.$$

From equation (4) since the assumptions of a perfect gas require the pressures to be proportional to the number of electrons per unit volume (n), it follows that

$$R\theta \log p_0 = R\theta \log p - e(V' - V) = R\theta \log P - w - e(V' - V)$$

and $R\theta' \log p' = R\theta' \log P' - w'$

where P and P' are the pressure of the free electrons within the metal. Consequently

$$e \int_{\theta'}^{\theta} \frac{\sigma}{\theta} d\theta - R \log \frac{P'}{P} - \frac{R\gamma}{\gamma-1} \log \frac{\theta}{\theta'} = 0,$$

and on differentiation with respect to θ ,

$$\sigma = \frac{1}{e} \left\{ \frac{R\gamma}{\gamma-1} - R\theta \frac{\partial}{\partial \theta} \log \frac{P}{P_1} \right\}$$

where P is the pressure of the internal free electrons at temperature θ , and P_1 is the value of the same quantity at some fixed temperature say θ_1 , and is thus a characteristic of the substance.

Since $P \propto n\theta$ where n is the number of free electrons per unit volume, this equation may be written

$$\sigma = \frac{1}{e} \left\{ \frac{R}{\gamma-1} - R\theta \frac{\partial}{\partial \theta} \left(\log \frac{n}{n_1} \right) \right\}$$

and since the electrons are considered as forming a perfect monatomic gas, for which $\gamma = \frac{5}{3}$, this becomes

$$\sigma = \frac{1}{e} \left\{ \frac{3R}{2} - R\theta \frac{\partial}{\partial \theta} \left(\log \frac{n}{n_1} \right) \right\} \quad . \quad . \quad . \quad (8)$$

Strictly speaking this expression does not really give the Thomson Coefficient, because the latter refers essentially to a steady current, whilst the above process deals with the transference of electrons under equilibrium conditions. But in the simple theory any slight differences of this kind are ignored, and the above equation gives the Thomson Coefficient.

When the above expression is compared with the facts it is found that the first term on the right-hand side of the equation, namely $\frac{3R}{2e}$ is very much greater than the observed values of σ , and hence, as was first pointed out by Thomson, the two terms within the bracket must be very nearly equal if the theory be correct, and we have therefore:

$$\log n = \frac{3}{2} \log \theta + a \text{ constant.}$$

So that n varies as $\theta^{\frac{3}{2}}$, or, in other words, the number of free electrons is required to vary very rapidly with the temperature.

From the equations for the Thomson and Peltier Coefficients we can readily deduce an expression for the thermo-electric force of a circuit by considering two metals with junctions at θ_1 and θ_2 , and imagining electrons to move round the circuit without leaving the metal. In this case subject to the assumptions which we have previously noted (p. 172) we have:

$$= P' - P + \int_{\theta_1}^{\theta_2} \sigma_2 d\theta + \int_{\theta_2}^{\theta_1} \sigma_1 d\theta,$$

where E is the electromotive force of the circuit, P' and P are the Peltier Effects at the two junctions, and σ_1 and σ_2 the Thomson Coefficients for the two metals.

Substituting the values previously deduced for the Peltier and Thomson Effects, we find on integration

$$E = \frac{R}{e} \int_{\theta_1}^{\theta_2} \log \frac{n_2}{n_1} d\theta \quad . \quad . \quad . \quad (9)$$

and

$$\frac{dE}{d\theta} = \frac{R}{e} \log \frac{n_2}{n_1} \quad . \quad . \quad . \quad . \quad .$$

These are the expressions for the thermo-electromotive force and its first differential coefficient, the latter, of course, giving the Peltier Effect in electrical units. For most pure metals, however, $\frac{dE}{d\theta}$ is nearly a linear function of the temperature, and this cannot be reconciled with both the above equations and that deduced from the Thomson Effect, since the latter requires n to vary as a simple power of θ .

REFERENCE

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6. Galvano-Magnetic and Thermo-Magnetic Phenomena

The free electron theory is not particularly successful in accounting for the galvano-magnetic and thermo-magnetic phenomena, and in fact the very complex nature of these, as shown by the variation of sign of the effect in different metals, and in some cases even with the magnitude of the field strength, is in itself strongly suggestive that the ultimate explanation will be far from simple.

The first suggestion made was that, in the case of the Hall Effect, the magnetic field acts on the electrons in the free paths between their collisions. If this be so, then if H be the strength of the magnetic field, u the velocity of average drift of the electrons in the direction of the electric force, and e the electronic charge, the average force acting on the electrons will be Heu , if we assume that the magnetic field does not appreciably alter the length of the time between two collisions, so that u remains constant. This force will act at right angles to the magnetic field and at right angles to the flow of the current.

This simple suggestion is, however, unsatisfactory for two reasons. In the first place it indicates that the effect should be directly proportionate to the field strength, which is not so. In the second place, and much more seriously, this theory will require the Hall Effect always to act in the same direction, whereas, as we have already seen, the Hall Coefficients are positive in some metals, and negative in others.

Various secondary hypotheses have been introduced in order to account for these phenomena, but none is particularly satisfactory or convincing. It has been suggested that the magnetic

field acts not only upon the electrons in their free paths, but also upon the atoms in such a way that the electronic collisions are affected. That is to say the magnetic field may distort the orbits of the electrons which remain bound to the atoms, so that the field of force surrounding an atom is changed. If this be so, the Hall Effect will be composed of two distinct processes, the action of the magnetic field upon the electrons in their free paths, and the action of the field on the atoms. Since these effects may not have the same sign, we can understand the complex nature of the phenomena. These explanations are, however, purely qualitative.

7. Discussion

In discussing the simple electron-gas theory it is necessary to distinguish carefully between the qualitative and the quantitative aspects. Considered qualitatively the theory gives a satisfactory explanation of many of the electrical properties, although it fails in connexion with supra-conductivity, the effect of pressure on resistance, variations in the Wiedemann-Franz ratio, and the fall in conductivity when a solid solution is formed.

As regards supra-conductivity, it seems almost inevitable that no simple conception of an electron gas will account for the phenomenon. Even the conception of electrons moving in guided paths or channels between the atoms appears insufficient to account for supra-conductivity in closed rings of polycrystalline metal, and it seems almost essential to conceive of some mechanism whereby the electrons can be passed on from one atom to another. But any conceptions of this kind are, of course, incompatible with the quantitative side of the theory in which the electrons are treated as particles of an ideal gas.

The fact that the electrical resistance is diminished by hydrostatic pressure is in contradiction to the simple theory, which is also unable to account for the variations in the Wiedemann-Franz ratio where these are larger than can be ascribed to the non-metallic part of the thermal conductivity.

The theory is also unsuccessful in accounting for the marked fall in conductivity which takes place when a pure metal forms a solid solution. This was originally considered as the result of thermo-electric forces between separate particles of the two metals, but now that it is known that solid solutions consist of the two kinds of atoms situated on a common lattice, this explanation has had to be rejected. The whole of the effect has to be ascribed either to marked changes in the numbers of the free

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electrons, for which there appears to be no reason, or to variations in the lengths of the free paths. The latter explanation is taken up in the theories of Wien, Lindemann, etc., but it naturally involves the rejection of much of the quantitative side of the theory which is based on the conception of an ideal gas.

It will be noticed that in the preceding sections we have made little or no reference to the numbers of free electrons or to the lengths of their free paths which are necessary in order that the equations may fit the facts. Since the electrical conductivity varies inversely as the temperature, it can be seen from the equation deduced for the conductivity, $C = \frac{ne^2\lambda v}{6R\theta}$, that

$\theta^{-\frac{1}{2}}$, since the kinetic theory requires the electron velocity v to vary as $\theta^{\frac{1}{2}}$. The equation for the Peltier Effect, $P = \frac{R\theta}{e} \log \frac{n_2}{n_1}$, indicates that the number of electrons per unit volume in different metals must be of the same order of magnitude, whilst the equation for the Thomson Effect, $\sigma = \frac{R}{e} \left(\frac{3}{2} - \theta \frac{d \log n}{d\theta} \right)$, requires

$n \propto \theta^{\frac{3}{2}}$ since σ is small compared with $\frac{3R}{2e}$. So far, however, we

have only relations connecting n and θ , or expressing the value of n λ , and we have not obtained any method of estimating n directly. The first of these methods was obtained from measurements of the optical properties of metals, and was developed by Schuster in 1904, the idea having been suggested by Drude in his original paper. The methods depend upon the fact that in deducing the fundamental equation for electrical conductivity we assumed that the electric force acted on the electrons for the whole of the time between two collisions. Consequently when we come to deal with periodic electric forces, in which the frequency is high, and the period so short as to be comparable with the time between two electronic collisions, the fundamental formulae require modification. In the reflection of visible light, or of infra-red radiation, corresponding to rapidly fluctuating electric forces, the portion of the light absorbed is intimately connected with the conductivity of the metal under these conditions. In this way by comparing the conductivity of the metal under ordinary conditions, with the conductivity under the influence of light waves of known frequency, we can obtain an indication of the time between two electronic collisions, and hence of the number of electrons present.

The first theoretical investigation was due to Schuster,¹ and indicated that the number of free electrons present was from one to three times the number of atoms, and the later work confirmed the same general conclusion that the number of free electrons was of the same order as that of the atoms. As pointed out later by Livens,² the method is not accurate enough to determine anything more than the general order of magnitude, and attempts made to calculate the exact numbers of free electrons per atom are unjustified.

The conclusion that the numbers of free electrons are of the same order as those of the atoms is quite reasonable, since the facts of chemistry indicate clearly that the atoms of metals readily lose one, two, or sometimes three electrons to form salts or other ionized compounds. The ease with which the electron will be lost inside the solid metal is, however, a matter of some doubt, because although the so-called *ionization potentials* are a measure of the energy required to remove an electron from a metallic atom, they refer essentially to free atoms in the gaseous state, and are not applicable to conditions inside a solid metal.

On the whole we should expect one of two alternatives, the first of which is that each atom should lose a definite number of electrons, and that these numbers should be independent of temperature over considerable ranges. In this event, the general facts of physics and chemistry will in many cases enable us to limit strictly the possible numbers of free electrons. In the case of the alkali and alkaline earth metals, for example, it is most improbable that more than one and two electrons per atom respectively will be free, since any further ionization would have to result in the breakdown of the very stable electron groupings corresponding to the inert gases.

The obvious disadvantage of the conception that the number of free electrons is some simple multiple of that of the atoms, is that in this case the total number of electrons in a piece of metal will be constant, and it is difficult to reconcile this with the equations in which the comparatively small thermo-electric effects require a rapid variation of n with θ if the correct order of magnitude is to be obtained. Further, if n is practically independent of θ , the equations for the conductivities indicate that $\lambda \propto \theta^{-\frac{1}{2}}$ since the electron velocity v varies as $\theta^{\frac{1}{2}}$, and such a rapid variation of λ with θ seems incompatible with the simple method of calculation in which the electrons are treated as particles of a gas.

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The alternative is that the number of free electrons varies with the temperature so that there is a balanced equilibrium of the type

Metal atom \rightleftharpoons Metal ion + Free electron.

In this case if Q is the heat of dissociation of the atom, i.e. the work required to remove the electron, the fundamental laws of thermodynamics lead to the following relation between n and θ .

$$n = n_0 e^{-\frac{Q}{R\theta}}.$$

This expression is independent of any particular mechanism of dissociation, and involves merely the energy change.

We now, however, come to the real fundamental difficulty of the whole theory, which is that if the number of electrons is of the same order as that of the atoms, we are at a complete loss as to how to account for the specific heats. For if we assume the principle of equipartition of energy, and put the kinetic energy of an electron as $a\theta$, then, when the metal is heated, we have to supply the energy, not merely to the atoms, but also to the free electrons. Further, any change in the number of electrons produced by a rise in temperature will be in the direction of heat absorption (since Q in the relation $n = n_0 e^{-\frac{Q}{R\theta}}$ is positive), and this effect will make the observed specific heat still larger. But the actual specific heats can be completely accounted for at ordinary and low temperatures by considering the energy necessary to raise the temperature of the atoms alone, and hence, if the simple electron-gas theory be true, there cannot be more than one electron to every hundred atoms. There is no escape from this conclusion. If once we write the kinetic energy of a free electron as $a\theta$, we are bound to assume that the kinetic energy of each free electron will increase as the temperature is raised.

There are two obvious ways of escape from this impasse. On the one hand we may give up the equipartition theory, and assume that the velocity of the electrons does not increase with temperature. In this case we have to give up the whole of the quantitative side of the theory which is based on the treatment of the electrons as though they were particles of an ideal gas, with the result that the theory becomes little more than a general qualitative explanation. We are not justified in assuming the kinetic theory, and in writing the kinetic energy of an electron as $a\theta$, where it happens to lead to the correct result, and then conveniently ignoring it when it conflicts with the specific heats.

Attempts of this sort are little more than the methods of the schoolboy who 'cooks' his calculations to produce the right answer.

Alternatively we may accept the evidence of the specific heats, and assume that the number of conducting electrons is small compared with that of the atoms, in which case the evidence based on the optical properties has to be ignored, but apart from this we are led into difficulties in connexion with the temperature coefficients. For if the relation between the number of free electrons and the temperature is of the type

$$n = n_0 e^{-\frac{Q}{R\theta}}$$

the number of electrons must diminish very rapidly at low temperatures, and, since the conductivity increases, the lengths of the free paths will have to be thousands or even millions of times the inter-atomic distances. Even if Q be not a constant, but varies with the temperature, this difficulty will still arise, because as long as work is needed to remove an electron from an atom, n will still diminish at low temperatures.

Experimentally there is much evidence that the free paths are large in comparison with the inter-atomic distances (see p. 339), but it is clear that a conception of long free paths of this magnitude is incompatible with the simple 'gas' theory in which the electrons are treated as particles of an ideal gas moving freely between the atoms, and colliding with them more or less at random, so that the simple kinetic theory can be applied.

Apart from these major difficulties there are other minor inconsistencies between the different equations required by the Drude theory if these are to agree with the facts. The one great triumph of the theory is the prediction of the Wiedemann-Franz ratio, but apart from this the quantitative side leads to such hopeless inconsistencies, particularly as regards the specific heats and free paths, that it is now generally rejected. Historically, however, it is of the greatest interest and importance. It was a bold and sweeping attempt to cover all the electrical properties of metals by one simple assumption, and although the assumption was certainly much too simple, the success attained was very striking, even though the quantitative development soon began to create more difficulties than it solved.

REFERENCES

1. Schuster. *Phil. Mag.* 1904, 7, 151.
2. Livens. *Phil. Mag.* 1915, 30, 112.

THE OLDER COMPLEX ELECTRON-GAS THEORIES

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1. General

THE theory of Drude, which we have described in the previous chapter, was the first real attempt to give a quantitative explanation of the electrical and thermal properties of metals, and it was only natural that it should have been extended in many directions. The literature of the subject is very extensive, but, in general, the different investigations may be said to divide themselves into two classes. On the one hand innumerable attempts were made to remove the crude simplifying assumptions of the Drude theory, and to replace these by more detailed conceptions. The Drude theory, for example, assumed that the electrons all had the same velocity v , whilst in the later work this admittedly crude assumption was removed, and the electron velocities were considered to be distributed over a wide range according to the Maxwell Distribution Law. These developments of the theory involved a large amount of highly ingenious mathematical work, but the net result was very disappointing, and removed none of the fundamental objections inherent in the original Drude theory. But, on the other hand, great advances were made by applying the principles of statistics and thermodynamics to the equilibrium between the electrons inside a metal, and those in the surrounding space, and in this way general equations were deduced in connexion with thermionic emission, contact potentials, &c. In this part of the work, the difficulties concerning the specific heats and free paths of the electrons were to a great extent ignored, although in some cases it was necessary to introduce terms for the specific heat of the electrons inside a metal. The general result was thus a very confused position in which great progress appeared to be made in one direction, whilst all the difficulties in connexion with the specific heats and free paths still remained unsolved.

2. The Lorentz Conductivity Equations

In the simple theory of Drude the electrons are considered to have a constant velocity v , which is connected with the temperature by the relation $\frac{1}{2}mv^2 = a\theta$, this relation being that of the simple kinetic theory of gases. In the later more complex theories, this admittedly crude assumption is replaced by the conception of electrons with velocities distributed over a wide range, the actual distribution assumed being that given by the Maxwell Distribution Law. According to this law, if ξ, η, ζ are the velocity components of an electron parallel to three rectangular co-ordinates (x, y , and z), the number of electrons per unit volume whose velocities lie between the limits (ξ, η, ζ) and $(\xi + d\xi, \eta + d\eta, \zeta + d\zeta)$ is given by the expression

$$N \sqrt{\frac{q^3}{\pi^3}} e^{-q^2} d\xi d\eta d\zeta,$$

where N is the total number of electrons per unit volume,

q is a constant connected with the mean square of the velocities u_m , by the relation $q = \frac{3}{2u_m^2}$.

This expression therefore gives the velocity distribution of the electrons in the absence of an external electric force, and the problem then consists in finding how this distribution will be affected when an electric force is applied so that the electrons acquire a general drift in the direction of the force. Just as, in the Drude Theory, we assumed a constant electron velocity v in the absence of an electric force, and then imagined the electrons to acquire a general drift u when an electric force was applied, so, in the more complex theories, we imagine the Maxwell Law to give the normal distribution of electron velocities, and calculate how this distribution will be affected if the electrons acquire a slight drift in one direction when an external electric force is present. This problem has been approached from many angles, but, when properly applied, the different methods are in agreement, and fall generally into two classes.

In the line of approach adopted by Thomson,¹ Jeans,² Wilson,³ Livens,⁴ and Bohr,⁵ it is assumed that the electric force acts on the electrons in the free paths between their collisions with the atoms, but that each collision destroys the whole effect of the

force during the previous free path, so that the electron starts off after each collision with the velocity which it would have according to the Maxwell Law. At any given instant therefore, the Maxwell Law gives, not the distribution of the velocities at this instant, but their velocities at the beginning of the free paths being pursued at the particular instant, the exact time at which the free paths were started being different for the different electrons. It has been argued by Livens that some assumption of this kind must be made in order to ensure the possibility of anything in the nature of a steady state for the velocity distribution under a uniform electric force.

On the basis of the above assumption, it is possible to deduce an expression for the actual velocity distribution at any instant, and this expression is identical with that given by the method of Lorentz,⁶ in which it is assumed that the Maxwell Law gives the velocity distribution of the electrons in the absence of the electric force, and that, when an electric force is applied, a new *steady state* is set up, in which the distribution differs but slightly from that given by the Maxwell Law. This slight difference is then calculated from statistical considerations regarding the effect upon the distribution of the electric force on the one hand, and of collisions with the atoms on the other.

In order to understand the methods used here, it is necessary to introduce the conception of a velocity diagram which was first used by Maxwell. At any given instant each molecule of a gas, or, in our particular problem, each electron of the electron gas, will have a certain velocity in a certain direction, and we may resolve this into three components ξ , η , ζ , parallel to the x , y , and z axes to which we refer the position of the electrons. We may now imagine a diagram to be drawn in which we again have three rectangular axes, but where these refer, not to the positions in space of the electrons, but to their velocities parallel to the x , y , and z axes, so that if an electron has *velocity* components ξ , η , ζ in the metal, it will be represented in the diagram by a point with *linear* co-ordinates ξ , η , ζ . In this way all the different velocities of the electrons in space will be represented by innumerable points in the so-called *velocity diagram*, and the distribution of these points round the origin gives a measure of the velocity distribution of the electrons. As long as there is no resultant flow of electrons in any one direction, the points in the velocity diagram will be situated perfectly symmetrically round the origin, but if the electrons acquire a small general drift in

one direction, the points will be slightly displaced in the velocity direction concerned.

For convenience we deal with a cylindrical conductor, in which the electric force E acts in the direction of the axis, and we refer the positions of the electrons to three axes x , y , and z , of which x is parallel to the axis of the cylinder. In this case, if a potential difference exists between the ends of the cylinder, the electrons will be subject to an acceleration in the direction of the x axis, and the velocity points in the velocity diagram will be displaced along the ξ axis.

Now let $d\lambda$ be an element of volume in the velocity diagram, situated at the point (ξ, η, ζ) and so small that we can neglect the changes of ξ, η, ζ from one of its points to another, and yet so large that it contains a great number of velocity points. Then this number may be considered as proportional to $d\lambda$. Representing it by

$$f(\xi, \eta, \zeta)d\lambda \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

per unit volume of the metal, the function f will, from the statistical point of view, determine the motion of the swarm of electrons.

The integral

$$\int f(\xi, \eta, \zeta)d\lambda \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

extended over the whole space of the velocity diagram, will give the total number (N) of electrons per unit volume, and the integral

$$\int \xi f(\xi, \eta, \zeta)d\lambda$$

can be shown to represent the stream of electrons through a plane at right angles to the x axis; i.e. the excess of those passing in the positive direction over those in the negative direction, both numbers referring to unit area, and unit time.

If all the electrons carry equal charges e , the expression for the flow of electricity will therefore be given by

$$J = e \int \xi f d\lambda \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

whilst the flow of energy across the plane will be given by

$$W = \frac{1}{2} m \int \xi^2 f \cdot d\lambda \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where m is the mass of an electron, and $r^2 = \xi^2 + \eta^2 + \zeta^2$, so that $\frac{1}{2}mr^2$ is the kinetic energy of the electron, and as in the simple

theory the mean kinetic energy is equal to $a\theta$ where θ is the absolute temperature. These two quantities J and W are therefore the expressions for the flow of electricity and of heat, and it is necessary to determine the function f in the presence of an electric force.

For this purpose we may assume that the electrons are subjected to a force in the direction OX giving them an acceleration X . We may consider a group of electrons which, at the time t , lie in an element of volume dS in the metal, and which have their velocity points in an element $d\lambda$ of the velocity diagram. If there were no encounters, either with other electrons or with metallic atoms, these electrons would be found at the time $t+dt$, in an element dS' equal to dS , and lying at the point $(x+\xi dt, y+\eta dt, z+\zeta dt)$. At the same time, owing to the acceleration due to the force in the direction OX , their velocity points would have been displaced to an element $d\lambda'$ equal to $d\lambda$ and situated at the point $(\xi+Xd\lambda, \eta, \zeta)$ of the velocity diagram, so that we should have

$$f(\xi+Xd\lambda, \eta, \zeta, x+\xi dt, y+\eta dt, z+\zeta dt, t+dt) dS' d\lambda' \\ = f(\xi, \eta, \zeta, x, y, z, t) dS d\lambda \quad . \quad . \quad . \quad (5)$$

Actually, however, some of the electrons will have collided with atoms or with other electrons, so that the above expression is not quite correct, for some collisions will cause electrons, which at the time t were in the group ($dS d\lambda$), to leave this group, whilst other collisions will bring into this group electrons which were originally outside it. Hence the number of electrons which, at the time $t+dt$, constitute the group ($dS' d\lambda'$), is not the same as the number of those which at the time t belonged to the group ($dS d\lambda$), but is equal to this number minus the number of impacts which cause an electron to leave the group, and plus the number of impacts which bring a new electron into the group. Writing $adS d\lambda dt$ and $bdS d\lambda dt$ for these two numbers, we have after division by $dS d\lambda = dS' d\lambda'$

$$f(\xi+Xd\lambda, \eta, \zeta, x+\xi dt, y+\eta dt, z+\zeta dt, t+dt) \\ = f(\xi, \eta, \zeta, x, y, z, t) + (b-a)dt,$$

or since the function on the left-hand side may be replaced by

$$f(\xi, \eta, \zeta, x, y, z, t) + \left(\frac{\partial f}{\partial \xi} X + \frac{\partial f}{\partial x} \xi + \frac{\partial f}{\partial y} \eta + \frac{\partial f}{\partial z} \zeta + \frac{\partial f}{\partial t} \right) dt$$

we have

$$X \frac{\partial f}{\partial \xi} + \xi \frac{\partial f}{\partial x} + \eta \frac{\partial f}{\partial y} + \zeta \frac{\partial f}{\partial z} + \frac{\partial f}{\partial t} = b-a. \quad . \quad . \quad . \quad (6)$$

This is the general equation from which the distribution function f can be obtained if the terms a and b can be calculated. In order to calculate these terms it is assumed that collisions between electrons can be ignored in comparison with collisions between electrons and atoms, and also that the electrons and atoms collide as though they were rigid elastic spheres, the atoms being relatively of such greater mass that they may be considered as immovable.

We may first consider what will determine the number of electrons leaving the group $f(\xi, \eta, \zeta) d\lambda$ in equation (1), which gives the value of a in equation (6). For this purpose we consider first only those electrons in the group $f(\xi, \eta, \zeta) d\lambda$ in which, when a collision with an atom takes place, the line joining the centres of the atom and the electron, has, at the moment of impact, a direction lying within a small solid angle $d\omega$. The number of electrons in the group $f(\xi, \eta, \zeta) d\lambda$ which undergo an impact of this kind in the time dt , is then equal to

$$n R^2 f(\xi, \eta, \zeta) r \cos \theta d\lambda d\omega dt \quad . \quad . \quad . \quad (7)$$

where n is the number of atoms per unit volume,

R is the sum of the radii of an atom and an electron,

and θ is the angle between the direction of the electron velocity r , and the line joining the centres of the atom and the electron at collision.

We have next to consider how the collision will affect the direction of the electron's velocity, and it is here that the assumption of rigid spherical atoms and spherical electrons becomes involved. If the collisions are between spheres, the velocities before and after collision make equal angles with the line joining the centres at impact, and hence if (ξ, η, ζ) and (ξ', η', ζ') are the velocities of the electron before and after collision, the corresponding points in the velocity diagram lie symmetrically on opposite sides of a plane W passing through the origin of the velocity diagram, and at right angles to the axis of the cone $d\omega$, so that when the point (ξ, η, ζ) before the collision has different positions in the element $d\lambda$, the corresponding point after the collision will lie in an element $d\lambda'$ which is the image of $d\lambda$ in the plane W .

By integrating (7) over all values of ω which make acute angles with the direction of r , we therefore obtain a value for the term a of equation (6) representing the numbers of electrons thrown out of the group (1) on account of collisions.

Similarly, the above considerations concerning the relative positions of the velocity points before and after collision enable us to calculate the term b representing the number of electrons thrown into the group by means of collisions. For this the equation corresponding to (7) will be

$$n r^2 f(\xi', \eta', \zeta') r \cos \theta d\lambda d\omega dt \quad . \quad . \quad (7')$$

since $d\lambda' = d\lambda$, and $r = r'$ if r' is the velocity whose components are (ξ', η', ζ') , the line joining the centres making equal angles with r and r' .

Subtracting (7) from (7'), and integrating, we obtain the value of $(b-a)d\lambda dt$.

When the force which produces the acceleration X has a constant intensity, depending only on the co-ordinate x , there can exist a stationary state, in which the function f contains neither y nor z . Examples of this sort are when the ends of a cylindrical bar are kept at different temperatures, or when it is subjected to a longitudinal electric force. In such cases, on replacing $(b-a)d\lambda dt$ by the expression deduced from (7) and (7'), the fundamental equation (6) becomes

$$nR^2r \int \{f(\xi', \eta', \zeta') - f(\xi, \eta, \zeta)\} \cos \theta d\omega = X \frac{\delta f}{\delta \xi} + \xi \frac{\delta f}{\delta x} \quad . \quad (8)$$

In performing the integration we must leave ξ, η, ζ unchanged, so that r is a constant, but the values of ξ', η', ζ' will depend on the direction of the line joining the centres. Denoting by f, g, h the angles between this line (taken in such a direction that the angle with r is acute) and the axes, we have

$$\xi' = \xi - 2r \cos \theta \cos f, \quad \eta' = \eta - 2r \cos \theta \cos g, \quad \zeta' = \zeta - 2r \cos \theta \cos h.$$

So long as the state of things is the same at all points of the metal, the electrons will move equally in all directions, and we may assume the Maxwell Distribution Law which may be written in the alternative form

$$f(\xi, \eta, \zeta) = A e^{-q^2} \quad . \quad . \quad . \quad (9)$$

where q is the constant previously referred to and is equal to $\frac{3}{2u_m^2}$ where u_m is the mean square velocity, and, since we are assuming that the kinetic theory of gases applies to the electrons, $\frac{3}{2u_m^2} = a\theta$, so that

$$q = \frac{3m}{4a\theta} \quad . \quad . \quad . \quad (10)$$

From (9) the total number of electrons per unit volume is given by

$$= \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} q^3 \quad (10)$$

This relation, together with equation (10), shows the way in which the constants q and A depend upon the temperature and the number of electrons per unit volume.

The simple Maxwell Law will not, however, apply when an external force is present, or when the ends of a metallic bar are unequally heated. But if a steady state is set up there will always be definite values of N and u_m , and if we give q and A such values that $\frac{3}{2q}$ is equal to the mean square velocity, and

$A \sqrt{\frac{\pi^3}{q^3}}$ is equal to N , we may write the new distribution function in the form

$$f(\xi, \eta, \zeta) = Ae^{-q^2} + \phi(\xi, \eta, \zeta) \quad (11a)$$

where ϕ is a function which remains to be determined.

To do this, we have the fundamental equation (8), and, in addition to it, the conditions

$$\int \phi d\lambda = 0, \quad \int \phi r^2 d\lambda = 0$$

which must be fulfilled because the term Ae^{-q^2} has been so chosen that it leads to values of N and u_m^2 really existing.

The function ϕ represents the change which an external force or a difference of temperature produces in the velocity distribution. In general this change is very small compared with Ae^{-q^2} , so that on the right-hand side of equation (8) we may replace f by Ae^{-q^2} , the expression thus becoming

$$\begin{aligned} & \{ \xi', \eta', \zeta' - \phi(\xi, \eta, \zeta) \} \cos \theta d\omega \\ &= \left(-2qAX + \frac{dA}{dx} - r^2 A \frac{dq}{dx} \right) \xi e^{-q^2}. \end{aligned} \quad (12)$$

For this we may assume a solution

$$\phi(\xi, \eta, \zeta) = \xi X(r) \quad (13)$$

where X is a function of r alone. Substituting this in equation (12) we first find

$$\begin{aligned} \int \{ \phi(\xi', \eta', \zeta') - \phi(\xi, \eta, \zeta) \} \cos \theta d\omega &= X(r) \int (\xi' - \xi) \cos \theta d\omega \\ &= -2rX(r) \int \cos^2 \theta \cos f d\omega. \end{aligned}$$

Let us imagine two lines OP and OQ drawn from the origin of co-ordinates, the first in the direction of the velocity (ξ, η, ζ) , and the second in that of the line of centres at the moment of impact, the angle $POQ = \theta$ being acute. Denoting by μ the angle POX , and by ψ that between the planes POX and POQ , we have

$$\begin{aligned}\cos f &= \cos \mu \cos \theta + \sin \mu \sin \theta \cos \psi \\ \int \cos^2 \theta \cos f d\omega &= \int_0^{\frac{\pi}{2}} \int_0^{2\pi} \cos^2 \theta (\cos \mu \cos \theta + \sin \mu \sin \theta \cos \psi) \sin \theta d\theta d\psi \\ &= 2\pi \cos \mu \int_0^{\frac{\pi}{2}} \cos^3 \theta \sin \theta d\theta = \frac{1}{2}\pi \cos \mu = \frac{1}{2}\pi \frac{\xi}{r},\end{aligned}$$

by which (12) assumes the form

$$-\pi n R^2 \xi r \chi(r) = \left(-2qAX + \frac{dA}{dX} - r^2 A \frac{dq}{dX} \right) \xi e^{-ar^2},$$

showing (because ξ disappears on division) that our assumption really leads to a solution of the problem. If we put

$$\frac{1}{\pi n R^2} = l$$

the result is

$$\chi(r) = l \left(2qAX - \frac{dA}{dx} + r^2 A \frac{dq}{dx} \right) \frac{1}{r} e^{-ar^2}. \quad (14)$$

Finally, we find from (3) and (4) for the currents of electricity and of heat

$$\begin{aligned}J &= e \int \xi^2 \chi(r) d\lambda. \\ W &= \frac{1}{2} m \int \xi^2 r^2 \chi(r) d\lambda.\end{aligned}$$

In these formulae ξ^2 may be replaced by $\frac{1}{3}r^2$, and $d\lambda$ by $4\pi r^2 dr$; the integration is thereby reduced to one with respect to r from 0 to ∞ . Next substituting the value (14), and choosing $s = r^2$ as a new variable, we are led to the integrals

$$\int_0^\infty s e^{-qs} ds, \quad \int_0^\infty s^2 e^{-qs} ds, \quad \text{and} \quad \int_0^\infty s^3 e^{-qs} ds,$$

the values of which are

$$\frac{1}{q^2}, \quad \frac{2}{q^3}, \quad \text{and} \quad \frac{6}{q^4},$$

The two expressions (15b) and (15c) are thus the fundamental equations for the electrical and thermal conductivities according to the Lorentz statistical method. Both involve the term l , which as we have seen above is an abbreviation for $\frac{1}{\pi n R^2}$ where n is the number of atoms per unit volume, and R is the sum of the radii of an atom and an electron, or rather of their effective radii during the process of collision. As pointed out by Lorentz, this term may be considered as a kind of mean free path, but its identification in this way depends expressly upon the assumption that the problem can be treated as a kind of 'bullet-target' problem, in which the chance of any one given bullet (electron) hitting a target (atom) is proportional to the number of targets per unit volume (n), and to the cross-sectional area πR^2 . This necessarily means that the free path l shall not be markedly greater than the inter-atomic distances, if these are of the same order as the diameter of the spheres which the atoms are taken to resemble.

From these two expressions the value of the Wiedemann-Franz ratio is deduced as

$$\frac{K}{C} = \frac{\frac{8}{9} \sqrt{\frac{2}{3\pi}} a l N u}{\sqrt{\frac{2}{3\pi}} \cdot \frac{e^2 l N u}{a \theta}} = \frac{8}{9} \left(\frac{a}{e}\right)^2 \theta.$$

The value for the Wiedemann-Franz ratio deduced in this way is only two-thirds of that given by the simple Drude theory, and is therefore not in such good agreement with the actual experimental value, although the right order of magnitude is still maintained.

In the method of Lorentz described above we assume that in the collision process the atoms behave as elastic rigid spheres. The same method has been applied by Richardson⁷ to the more general case in which the law of force is of the form $\frac{K}{d^s}$ where d is the distance, and K is positive when the forces are repulsive. In this case the value for the Wiedemann-Franz ratio is

$$\frac{K}{C} = \frac{2s}{s-1} \cdot \frac{R^2}{e^2} \theta = \frac{8}{9} \frac{s}{s-1} \left(\frac{a}{e}\right)^2 \theta,$$

and the best agreement with fact is obtained by assuming $s = 3$, or in other words a repulsive force varying inversely as the cube

of the distance. These refinements did not, however, remove any of the real objections to the theory in connexion with the specific heats and free paths.

In the discussion on the Drude theory we have already indicated that the conductivity equations require modification when applied to periodic fields of high frequency such as are met with in connexion with the optical properties of metals. The application of the more complex theories to this problem has been discussed in great detail by Livens,⁴ and as in the simple theory, the general conclusion is that the number of free electrons is of the same order as that of the atoms.

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3. Thermo-Electric Effects

The method which we have described before (p. 170) in connexion with the Drude theory can also be used with the Lorentz theory since both require the mean kinetic energy of an electron to be equal to $a\theta$. In this way, if we make the same approximation as regards the transference of energy across a boundary, we obtain the same equations for the Thomson and Peltier coefficients, and for the thermo-electric power. To a higher degree of accuracy this method is no longer justifiable, because it assumes that the whole energy change which takes place when an electron crosses a boundary can be accounted for by the difference in potential on the two sides. In equilibrium conditions when no current is flowing this assumption is justifiable, but the Thomson and Peltier effects refer to conditions in which there is steady current, or in other words a stream of electrons, and under these conditions there will be a transference of kinetic energy when the electrons cross a boundary, unless it happens that the conditions of motion of the electrons are exactly the same on both sides of the boundary. If, for example, the law of force between an atom and an electron during a collision varies inversely as the n^{th} power of the distance in one metal, and as

the m^{th} power in another metal, a steady stream of electrons across the boundary will involve a transference of kinetic energy which, according to Bohr,¹ will be given by

$$\frac{2a\theta}{e} \left(\frac{n}{n-1} - \frac{m}{m-1} \right).$$

Consequently, the assumption which we made in deducing the Peltier coefficient, namely, that the energy change, when an electron crossed the boundary between two metals, could be expressed in terms of the potential differences under equilibrium conditions, is no longer justified when we deal with a steady current. Similarly, in obtaining the Thomson coefficient, the expressions deduced for the energy changes involved when an electron is removed from the metal to the surrounding space will require a term to represent the transference of kinetic energy, since the Thomson effect refers to a steady current, and not to the ordinary equilibrium conditions.

These effects have been discussed by Richardson,² Wilson,³ and Bohr, and more generalized expressions for the various coefficients have been obtained. Thus the equation for the specific heat of electricity becomes, according to Richardson,

$$= \frac{R}{e} \left\{ \frac{3}{2} - \frac{\theta}{R} \frac{d}{d\theta} \left(\frac{\lambda - \lambda_0}{\theta} \right) - \theta \frac{d \log n}{d\theta} \right\},$$

where the middle term in the bracket takes into account the transference of kinetic energy, λ being the energy transferred in unit time by unit electric current in the metal, and λ_0 that for the current outside. The equations for the Peltier coefficient and thermo-electric power may be modified in the same way so that more generalized expressions are obtained. We shall not, however, deal with these in detail because the λ terms cannot be estimated directly, and it is now generally recognized that the application of the classical laws to the electrons within a metal is unjustified.

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4. Emission Phenomena

The older electron-gas theories of Lorentz and others were not particularly successful in accounting for the emission phenomena as a whole, although they attained a considerable success when

restricted to thermionic emission. The principal difficulties met with in this connexion were the sharpness of the photo-electric threshold, and the temperature-independence of the photo-electric and strong field emission, although the last-named process was really only examined in detail after the Lorentz theory had been developed.

The general viewpoint adopted is that a definite amount of work has to be done by an electron to cross the surface, and that if the free electrons have sufficient energy they will be able to break through the surface of the metal, and hence that emission may be brought about either by raising the metal to a sufficiently high temperature, or alternatively by allowing the electrons to gain energy from some external source, as, for example, by the absorption of energy from light or other radiation. As we shall see later, this conception led to a satisfactory explanation of the thermionic emission, but appeared to be in direct contradiction to the photo-electric effect being independent of temperature. For the Lorentz, as well as the earlier Drude theory, requires the mean kinetic energy of the electrons to vary directly as the absolute temperature, so that we should expect the photo-electric emission to become continually greater as the temperature is raised.

In the same way the existence of a sharp photo-electric threshold appears incompatible with the Maxwell type of distribution law, in which the velocities are distributed symmetrically about the mean value.

As the result of these inconsistencies, the development of the theory was very confused, and a position was reached in which it was generally admitted that the electrons concerned in photo-electric emission existed in the metal in a condition such that their energy was not only independent of temperature, but was also constant, this last point being required to account for the sharpness of the threshold frequency. On the other hand, the thermionic electrons were regarded as obeying the Maxwell Law, so that the two emission processes were ascribed to electrons in different states. This position was clearly unsatisfactory, since we should naturally expect the free electrons to be those emitted most readily under any conditions. Fortunately these difficulties have to some extent been removed by the later theories of Sommerfeld and others, which are based on the new statistical methods, and in this chapter we shall therefore confine our attention to the general thermo-dynamic treatment of electron emission. The theoretical development of the subject was some-

times rather confusing, owing to the fact that terms with nearly, but not necessarily exactly, the same meaning were frequently interchanged by different writers.

We may consider first the conception of electron evaporation which has been frequently used in this connexion. In this case we consider a metal to be enclosed in a hot insulated chamber, and imagine that electrons evaporate until a state of equilibrium is reached in which the number of electrons leaving the metal in a given time is equal to the number which enter it from the vapour phase. We assume further that the electron atmosphere outside the metal is so dilute that the electrons can be regarded as obeying the simple gas laws, whilst the state of the electrons inside the metal remains unknown. Under these conditions, the application of the usual Clausius-Clapeyron treatment* indicates that at equilibrium the pressure of the electrons in the vapour phase will be given by the relation

$$p = k\theta Ae^{\frac{\phi}{k\theta}} \quad . \quad . \quad . \quad . \quad . \quad (16)$$

where ϕ is the latent heat of evaporation of the electrons, k is the Boltzmann constant, and A is a constant which is independent of the temperature, but which may depend upon the particular metal concerned.

Since the electron atmosphere is assumed to be a perfect gas, the kinetic theory enables us to calculate the number of electrons which strike unit area of the metal in unit time, and this is given by

$$n = \frac{p}{\sqrt{2\pi m k\theta}} \quad . \quad . \quad . \quad . \quad . \quad (17)$$

At equilibrium this, multiplied by $(1-r)$, must be equal to the number of electrons leaving the metal in unit time, where r is the fraction of electrons which strike the surface from the outside, and are reflected back without entering the metal. The number (N) of electrons leaving the metal per unit area per unit time *under equilibrium conditions* is therefore given by

$$N = (1-r) \frac{(k\theta)^{\frac{3}{2}}}{\sqrt{2\pi m}} \cdot Ae^{\int_0^{\theta} \frac{\phi}{k\theta^2} \cdot d\theta} \quad . \quad . \quad . \quad . \quad (18)$$

In the original rough development of the theory, the following general simplifying assumptions were then made.

* A description of this will be found in text-books of Physical Chemistry such as Nernst, *Theoretical Chemistry*, or Lewis, *A System of Physical Chemistry*.

- (1) The reflection of electrons at the surface of the metal was ignored, so that the term $(1-r)$ was omitted from the equation.
- (2) The latent heat of evaporation ϕ was assumed to be independent of temperature, so that the term $\int_0^\theta \frac{\phi}{k\theta^2} \cdot d\theta$ reduced to $-\frac{\phi}{k\theta}$.
- (3) It was assumed that the thermionic emission current under ordinary experimental conditions was the same as the number of electrons leaving the metal under the conditions of ideal equilibrium assumed in the Clausius-Clapeyron treatment, so that $N = I$, where I is the emission current.

When these simplifying assumptions are made, it can at once be seen that equation (18) reduces to the simple Richardson equation (see p. 140) of the type

$$I = a\theta^5 e^{-\frac{b}{\theta}}.$$

These simplifying assumptions are, however, unsatisfactory, for in the first place there is direct experimental evidence that considerable reflection of electrons takes place at the surface of a metal, whilst apart from this, the assumption of a constant value for ϕ is highly arbitrary. The further assumption that the steady emission current is the same as the number of electrons leaving the metal under equilibrium conditions is not strictly justified, but the error here is comparatively small (see p. 202).

The effect of variations of ϕ with θ have been discussed at length by many writers, and we may deal here with the simple thermodynamic method adopted by Dushman¹ and others. According to ordinary thermodynamic theory, the latent heat of evaporation of a solid or liquid varies with the temperature in a way which depends on the specific heats of the solid (or liquid) and vapour, the variation being given by the relation

$$\phi = \phi_0 + \int_0^\theta C_{p(\text{vapour})} d\theta - \int_0^\theta C_{p(\text{solid})} d\theta \quad . \quad (19)$$

which on combination with the Clausius-Clapeyron equation gives for the equilibrium vapour pressure

$$\log p = -\frac{\phi_0}{R\theta} + \frac{1}{R} \int_0^\theta \frac{\int_0^\theta C_{p(\text{vapour})} d\theta}{\theta^2} \cdot d\theta - \frac{1}{R} \int_0^\theta \frac{\int_0^\theta C_{p(\text{solid})} d\theta}{\theta^2} \cdot d\theta + B \quad (20)$$

where B is an integration constant, which, as shown by Sackur and others, may be expressed in terms of a fundamental constant i_0 , in the case of monatomic gases which an electron gas may be supposed to represent. The exact relation is

$$B = i_0 + \frac{3}{2} \log M$$

where M is the molecular weight of the gas particles, and the fundamental constant i_0 is given by

$$i_0 = \log \left(\frac{(2\pi)^{\frac{3}{2}} k^{\frac{5}{2}}}{N^{\frac{1}{2}} h^3} \right)$$

where k is Boltzmann's constant $= 1.372 \times 10^{-16}$ ergs/deg., N is Avogadro's number $= 6.06 \times 10^{23}$, and h is Planck's constant $= 6.55 \times 10^{-27}$ erg/sec.

In order to proceed further we have to know the specific heats of the electrons in the solid and vapour phase, and it is here that difficulties begin to arise. For the vapour phase the electrons may be legitimately considered as resembling a perfect gas, so that the value of $C_{p(\text{vapour})}$ is $\frac{5R}{2}$. If now we accept the Lorentz theory, the

specific heat of an electron inside the solid metal is again that of a perfect gas $\left(\frac{5R}{2}\right)$, so that the two specific heat integrals fall out of equation (20), and the latent heat of evaporation of the electrons becomes constant, and the emission formula again becomes of the form

$$I = (1-r) a \theta^{\frac{1}{2}} e^{-\frac{b}{\theta}}.$$

On the other hand, if we reject the Lorentz theory as regards the specific heats, and accept the experimental evidence that the specific heat of the electrons within the metal is negligible, we may put $C_{p(\text{solid})} = 0$, in which case equation (20) becomes

$$\log p = -\frac{\phi_0}{R\theta} + \frac{5}{2} \log \theta + i_0 + \frac{3}{2} \log M \quad . \quad (21)$$

or
$$p = \theta^{\frac{5}{2}} M^{\frac{3}{2}} e^{-\frac{\phi_0}{R\theta}} e^{i_0}.$$

Hence, substituting the value for i_0 , and using equation (18), the expression for the emission current becomes

$$I = (1-r) \left(\frac{2\pi k^2 m e}{h^3} \right) \theta^2 e^{-\frac{\phi_0}{\theta}} = (1-r) 60.2 \theta^2 e^{-\frac{\phi_0}{\theta}}. \quad (22)$$

If we now neglect electron reflection, this equation is of the type $I = C\theta^2 e^{-\frac{d}{\theta}}$ where C is a universal constant, and as we have already seen in Chapter VII, an expression of this kind is in agreement with the facts.

These thermo-dynamic methods are perfectly general, but they suffer from the disadvantage that we have to ignore the electron reflection in order to make them agree with the facts. We may now describe a slightly different method of approach which is also due essentially to O. W. Richardson.² In this we use the device already described in connexion with the simple theory of thermo-electricity (p. 173), and imagine two portions of the same metal A and A' , at temperatures θ and θ' , and connected by a thin rod of the same metal. A and A' are in evacuated chambers, and electrons can be transferred reversibly from one chamber to another by means of suitable piston and cylinder devices. Under these conditions A and A' acquire potentials V and V' and we surround A by a potential filter maintained at the potential V' , so that no work against electrical forces is done if we remove an electron from that part of the chamber at θ which is outside V' to the chamber at θ_1' . The effect of the potential filter V' will be to reduce the pressure of the electrons from the equilibrium value p characteristic of the metal at temperature θ , to a value p_0 where

if we assume that the pressure of the electrons obeys the simple gas law $p = nk\theta$.

We now imagine a given number of electrons to be taken out of the metal A at temperature θ (work done is w), transferred through the potential filter to pressure p_0 , expanded adiabatically to the temperature θ' , and then isothermally at θ' to the pressure p' , which is the pressure outside A' . After this they are allowed to condense in A' , and to run down the wire from θ' to θ . In this last process they will absorb an amount of heat proportional to $e \int_{\theta}^{\theta'} \sigma d\theta$, where σ is the amount of heat liberated when unit quantity of electricity flows down unit difference of temperature *under these experimental conditions*. This process, subject to the restriction mentioned later (page 202), forms a complete reversible cycle, and therefore applying the second law of thermo-dynamics in the form $\int \frac{dQ}{\theta} = 0$, we find, after calculating the amount

of work in each of the above processes, and putting γ for the ratio of the specific heats at constant pressure and constant volume,

$$\frac{w}{\theta} - \frac{w'}{\theta'} + k \left\{ \log p - \log p' - \frac{\gamma}{\gamma-1} (\log \theta - \log \theta') \right. \\ \left. + e \int_{\theta'}^{\theta} \frac{\sigma}{k\theta} d\theta \right\} = 0, \quad (23)$$

$$\text{or} \quad p = A\theta^{\frac{\gamma}{\gamma-1}} e^{-\frac{w}{k\theta} - e \int_0^{\theta} \frac{\sigma}{k\theta} d\theta} \quad (24)$$

The term σ in this equation is not exactly the same as the coefficient of the ordinary Thomson Effect, because the latter refers essentially to a steady flow of electricity, while the above method deals with a virtual displacement of electrons under equilibrium conditions (see p. 194). For the present, however, we may ignore this difference, and assume that σ is at least of the same order as the Thomson coefficient, in which case the term $e \int_0^{\theta} \frac{\sigma}{k\theta} d\theta$ is small compared with $\frac{w}{k\theta}$.

Now we have already seen that the application of the Clausius-Clapeyron treatment gives the equilibrium pressure p in the form

$$p = k\theta A e^{\int_0^{\theta} \frac{\phi}{k\theta^2} d\theta}$$

where ϕ is the internal latent heat of evaporation of the electrons. We are not for the present entitled to assume that the ϕ term in the Clausius-Clapeyron equation is identical with the w term used in connexion with the diagram on page 173, for in the one case the method assumes a continuous flow, and the surfaces are not charged and discharged by the passage of the electrons in and out, whilst in the Clausius-Clapeyron treatment the escape of the electrons leaves the metal charged. If we equate the right-hand sides of equations (16) and (24), and take logarithms, and differentiate with respect to θ , we obtain

$$\phi = w - \theta \frac{dw}{d\theta} + \frac{k}{\gamma-1} \theta - e\sigma\theta. \quad (25)$$

If now we neglect any slight difference between ϕ and w , this reduces to

$$\frac{dw}{d\theta} = \frac{k}{\gamma-1} - e\sigma. \quad (26)$$

If we now ignore the small effect of the term $e\sigma$, and put $\gamma = \frac{5}{3}$ for a perfect gas, we find

$$\frac{dw}{d\theta} = \frac{3}{2}k,$$

$$w = w_0 + \frac{3k\theta}{2} \quad (27)$$

Since we are assuming $\phi = w$, this means that $\phi = \phi_0 + \frac{3k\theta}{2}$, in which case by using the previous equations, we find for the emission current

$$I = (1-r) \frac{(k\theta)^{\frac{1}{2}}}{\sqrt{2\pi m}} \cdot Ae \int_0^{\theta} \frac{\phi_0 + \frac{3}{2}k\theta}{k\theta^2} \cdot d\theta$$

$$= (1-r) C \theta^2 e^{-\frac{\phi_0}{k\theta}} \quad (28)$$

which as we have already noted is in agreement with the facts if the reflection of electrons at the surface is ignored.

At this stage the reader may not unnaturally ask how it is possible to deduce equations of the type $\phi = \phi_0 + \frac{3k\theta}{2}$ for the variation of the emission constant, when no assumptions have been made as to the part which the metal itself plays in the process. For although the term ϕ_0 may vary from one metal to another, it would seem highly arbitrary to suggest that the temperature variation will always be $\frac{3k\theta}{2}$ irrespective of the crystal structure, the nature of the lattice forces, and similar factors. In order to answer this question it is necessary to consider the real limitations of the methods which we have described above.

In the first place it may be objected that it is unjustifiable to apply the various thermodynamic cycles to the electrons alone, without considering their interactions with the atoms. In other words, since the equilibrium between the solid metal and the vapour is really of the nature

$$[\text{atoms} + \text{electrons}]_{\text{solid}} \rightleftharpoons [\text{atoms} + \text{electrons}]_{\text{vapour}},$$

it may be argued that we have really no justification for dealing with cycles involving only the electrons and their specific heats in the two phases, and for ignoring the atoms as in equation (19) page 197. According to O. W. Richardson* this objection is unimportant, for, if attempts are made to deal with the whole system [atoms+electrons], the result is that a number of complicating terms are added at the beginning of the cycle, and subtracted at the end so that the final answer is unchanged.

* I have to thank Professor Richardson for explaining this point in detail in a private communication.

A much more serious limitation of the method is that in dealing with cycles such as that on page 199, we are dealing with cases in which the reversible effects are superimposed upon the irreversible flow of heat from one temperature to another. Thus in the figure on page 173, where the two pieces of metal are at temperatures θ and θ' , there is a continuous flow of heat down the connecting rod, and it is the *assumption* of the method that we can superimpose the reversible phenomena, and treat these thermo-dynamically, just as though the irreversible flow of heat were absent. This is the same assumption as that involved in the Kelvin theory of thermo-electricity, and it cannot be proved to be necessarily valid. The thermo-electric theory, however, gives results which are at least approximately correct, and since the thermo-electric quantities are, for all normal metals, of a much smaller order of magnitude than the thermionic constants, the method is presumably justified in connexion with emission phenomena. It will further be noted that on page 200, the method for obtaining the relation

$$\phi = \phi_0 + \frac{3}{2}k\theta$$

involved the rejection of the terms involving the (slightly modified) Thomson coefficient σ , and it is here that the second approximation is made. The obtaining of an expression independent of all constants of the metal, other than ϕ_0 , involves therefore the assumption that we can neglect quantities of the order σ , and in the case of all normal metals this is justified to a degree of accuracy exceeding that with which the constants can be determined.

As regards the possible difference between the terms w and ϕ involved in the two methods of approach used above, we have already deduced the equation (25) from which

$$w - \phi = \theta \frac{dw}{d\theta} \quad \gamma - 1$$

From a detailed examination of the very accurate results of Davisson and Germer³ on the cooling effect (see below), Richardson⁴ has shown that the right-hand side of this last equation cannot exceed $k\theta$ without contradicting the experimental evidence. Inserting the numerical values, this implies that the difference between w and ϕ cannot at the most exceed 0.23 volts, the value of w itself being of the order 4.9 volts. To within an accuracy of at least 5%, we are therefore justified in interchanging ϕ and w in the derivation of the equations, and the two may be identical.

The Bearing of the Emission Phenomena on the State of the Internal Electrons.

For many years it was thought that the emission phenomena supported a theory of the Drude-Lorentz type, since this enabled the prediction of the equation $I = a\theta^{\frac{1}{2}}e^{-\frac{b}{\theta}}$, which agreed reasonably well with the facts. It was, however, shown later by Richardson⁴ that the accurate data of Davisson and Germer were really in better agreement with a theory in which the energy of the electrons inside the solid metal was independent of temperature. These investigators measured the 'cooling effect' during emission, and we may denote this by L so that if E is the mean kinetic energy of an internal electron

$$L = 2k\theta + \xi - f(E),$$

where ξ is the difference in potential energy of an electron inside and outside the metal, $2k\theta$ its kinetic energy leaving the surface, and $f(E)$ denotes the kinetic energy of the electrons flowing in the stream inside the metal. The function $f(E)$ depends not only on the mean kinetic energy of an electron in the metal, but also on the law of force controlling the collisions, so that it is different if the atoms and electrons collide as hard spheres, or according to some other law. From the point of view of the Lorentz theory, $E = \frac{3}{2}k\theta$, and $f(E) = \frac{2n}{n-1}k\theta$, where n is the index in the law of force d^{-n} assumed during the collisions. According to the classical theory therefore

$$L = 2k\theta + \xi - \frac{2n}{n-1}k\theta$$

The internal latent heat of evaporation, w , is the difference in the internal and external energies under equilibrium conditions, and since $\frac{3}{2}k\theta$ is the energy in the vapour phase

$$w = \frac{3}{2}k\theta + \xi - E,$$

so that according to the Lorentz-Drude type of theory the cooling effect L is

$$L = w + 2k\theta - \frac{2n}{n-1}k\theta. \quad . \quad . \quad . \quad . \quad (29)$$

On the other hand, if the kinetic energy of the conducting electrons is independent of temperature, we may put $E = C_1$ and $f(E) = C$, so that in this case

$$L = w + \frac{1}{2}k\theta - C + C_1.$$

The two terms C and C_1 may be expected to be equal either for $E = 0$, or for cases where E is constant for the greater number of free electrons, or for cases in which the rate of transference is unaffected by E . These possibilities cover all likely types of non-classical theory, so that we have

$$L = w + \frac{1}{2}k\theta. \quad . \quad . \quad . \quad . \quad . \quad (30)$$

For any probable law of force, equation (29) cannot make L greater than w , whilst (20) requires L always to be greater than w , and actually the values found by Davisson and Germer agreed with equation (30) to within the limits of accuracy of the methods. The detailed examination of the emission phenomena thus eventually provided evidence against the Lorentz-Drude type of theory although the conclusions were at first in the opposite sense.

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4. Richardson. *Proc. Roy. Soc.* 1924, **A. 105**, 387.

5. Discussion

As will be appreciated from the above description, the older complex electron-gas theories led to an impasse from which there appeared to be no escape. In spite of all the mathematical ingenuity displayed in the complex theories, the real difficulties inherent in the simple Drude theory remained unsolved, and, while at first the general thermo-dynamic theory of emission appeared to favour the Drude-Lorentz conception of an electron gas obeying the classical laws, the later developments again indicated that the specific heat of the free electrons must be practically zero. In many directions there was undoubtedly a tendency to elaborate the mathematical analysis to an extent which was certainly unjustified in view of the obvious simplifications which underlay the assumptions of an electron 'gas'. But apart from criticisms of this kind it became increasingly apparent that an electron gas obeying classical laws could only be reconciled with the facts, if the number of free electrons was very small compared with that of the atoms. This required a rejection of the results obtained from a consideration of the optical properties, and also necessitated such long free paths that it seemed

impossible to justify the methods of calculation used. As was pointed out by Bridgman at the Solvay Congress, there is considerable evidence that the free paths are long, so that the difficulty here is not really one of fact, but is rather to see how such long free paths can be reconciled with the methods of calculation which are used in the 'electron gas' theories. As long as the problem was looked at from the point of view of bullet-like electrons moving among comparatively large atoms which behaved like elastic spheres during the collision process, the conclusion appeared inevitable that free paths of hundreds and thousands of times the interatomic distances were quite inadmissible, and from this point of view the theory broke down completely.

On the other hand, many physicists were reluctant to give up a theory which had achieved such a remarkable success in the prediction of the Wiedemann-Franz ratio, and the result was a very confused position in which the older theory was retained in some connexions and dropped in others. In order to overcome this difficulty a number of tentative theories were introduced which will be considered in the next chapter. In the majority of cases these were really qualitative only, but in order to fit in with the Wiedemann-Franz Law a number of additional assumptions were made, by means of which a constant ratio of the thermal and electrical conductivities was maintained, although the methods used were open to criticism. These theories gradually led up to the conception of the electron lattice theory which is considered in Chapter XII, and which received support from quite another direction, the problem of compressibility and lattice energy. As regards the electrical properties, little real quantitative progress was made by these theories, and the whole subject was rather neglected until the rapid developments which followed the introduction by Sommerfeld of the new statistical methods, and gave rise to a completely new theory which is described in Chapter XIII.

XI

INTERMEDIATE THEORIES

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1. The Di-Pole Theory of J. J. Thomson

THIS theory was put forward by Thomson as long ago as 1907,¹ and was subsequently extended in 1915 in a paper in the *Philosophical Magazine*,² the main object being to remove some of the difficulties inherent in the older 'electron gas' theories, particularly in connexion with the problem of supra-conductivity. The theory aroused great attention in its time, but as it is now of little but historical interest we shall only indicate very briefly the point of view adopted.

The theory is based on the assumption that the atoms or molecules of solid metals consist of electrical doublets or di-poles, each containing a pair of equal and opposite charges at a small distance apart. In the normal state the axes of these doublets are supposed to be distributed at random owing to the thermal vibrations of the atoms, but when an electric force is applied the axes of the doublets will tend to point in the direction of the force, just as a number of small magnets tend to point in one direction in a magnetic field. These polarized doublets will give rise to local fields which will be very much stronger than the external electric field, and the conductivity is regarded as due to the electrons being passed on from one di-pole to another, but the electrons which move are not those which give rise to the di-poles. From this point of view the difference between a metal and a non-metallic substance is not so much that the one has a greater tendency to form di-poles than the other, but rather that the metal contains free electrons which can be passed along the chains of di-poles, whereas the non-metallic substances contain no free electrons.

In the presence of an electric force there is thus a tendency for the di-poles to arrange themselves in chains, and this is opposed by factors such as the forces of the crystal lattice, the thermal vibrations, &c. The actual electric force acting on the di-poles

of moment M is not, however, equal to the external force X_0 , because the polarized doublets themselves will give rise to strong electric forces, and the total force acting on the di-poles, which we may denote by X , may be written

$$X = X_0 + kI$$

where I is the resultant of the moments of the di-poles in the direction of the electric force, since we may reasonably assume that the forces due to the di-poles themselves are proportional to I . In the case of the di-poles in a solid, the value of I will be some function of $\frac{XM}{D}$, where XM is the deflecting couple acting on the di-poles, and D is the restoring couple brought into play when the axis of the di-pole is deflected through unit angle. The nature of this restoring couple is not known, but at ordinary temperatures it is assumed to be proportional to $R\theta$, and by considering the conditions under which electrons are likely to be passed along the di-poles, the following expression is obtained for the electrical conductivity

$$C = \frac{epd NMC'}{R\theta - NM^2kC'}$$

where e is the charge on an electron, p the number of times per second that an electron is passed on from one atom to another, d the distance between the centres of two di-poles in a chain, N the number of di-poles per unit volume, and C' is a constant depending on the function $f\left(\frac{XM}{R\theta}\right)$ connecting I with $\frac{XM}{R\theta}$.

This expression is very complex, and in the original derivation of the theory two simplifying assumptions are made. The first assumption is that the di-poles themselves consist of charges $+e$ and $-e$, and the second assumption is that the free electrons which pass down the chains are themselves in thermal equilibrium, so that their mean kinetic energy is $R\theta$. In this way the following expressions are obtained for the electrical and thermal conductivities.

$$C = \frac{2}{9} \frac{e^2 p d n l}{R\theta}$$

$$K = \frac{1}{3} n d^2 p R$$

Here l is the distance between the charges in a doublet, and in a metal where the doublets will be so numerous as to be almost in contact, d and l will be nearly equal, so that the expression for

the Wiedemann-Franz ratio reduces to

$$\frac{K}{C} = \frac{3}{2} \frac{R^2 \theta}{e^2}$$

as compared with the value $\frac{4}{3} \frac{R^2 \theta}{e^2}$ required by the theory of

Drude. This apparently satisfactory agreement, however, depends expressly upon the assumption that the di-poles consist of charges of $+e$ and $-e$ separated by a distance approximately equal to the inter-atomic distances in the metal, so that a very marked degree of polarization is required.

The supra-conductivity phenomena are explained on the assumption that when the di-poles are formed into chains by the application of an external electric force, they are held together, not merely as the result of the external force, but also by the forces between the di-poles themselves. This tendency to keep orientated in a definite direction is then opposed by the thermal vibrations and the inter-atomic forces of the crystal lattice. We may now suppose that a current is started in a metal at a temperature so low that the thermal vibrations can be neglected, and may consider what will happen if the electric force is withdrawn. On the one hand, the forces between the di-poles will tend to keep them orientated in definite chains, whilst on the other hand the forces of the crystal lattice will tend to restore them to their original arrangement. Consequently if the lattice forces are the stronger, the chains of di-poles will break up on the removal of the electric force, and supra-conductivity will not be shown, whilst if the forces between the di-poles are the stronger they will remain in chains after the removal of the electric force, and the current will continue indefinitely, since it is one of the essentials of the theory that the electrons are passed on from one di-pole to another by the forces in the di-poles themselves, and not by the external force. Now let us suppose that the temperature is gradually raised, so that thermal vibrations are introduced. Supra-conductivity will continue as long as the restoring forces due to the di-poles are greater than the combined effects of the thermal vibrations and the forces of the crystal lattice, but directly this combined effect becomes the greater, the chains of di-poles will begin to break up. In this way the theory accounts both for the fact that the supra-conductivity appears sharply and that it is only shown by some metals.

The theory explains the effect of pressure on resistance, since

the more tightly the di-poles are pressed together the more readily will the free electrons be handed on from one di-pole to another. It can also be made to cover the galvano-magnetic and thermo-magnetic phenomena by assuming that, when the electric force is applied, the di-poles swing round into its direction, but that the axis about which the di-pole moves is not mid-way between the charges, so that when the motion takes place in a magnetic field, the doublets are deflected in one direction, thus giving rise to the Hall Effect. The thermo-electric properties are explained by assuming that the electrons are passing from one di-pole to another even in the absence of an electric force, but that, owing to the difference in the nature of the di-poles, the conditions of motion of the electrons are not the same in all metals, so that, when two metals are in contact, electrons tend to flow from one to the other.

The theory is thus extremely ingenious, but the conception of di-poles of such marked polarity leads to so many difficulties that the theory is now generally rejected. The prediction of the Wiedemann-Franz ratio depends expressly upon the assumption that the kinetic energy of the electrons is equal to $R\theta$, and this, of course, is a purely *ad hoc* assumption. In the free electron gas theories in which the electrons were regarded as behaving like gas molecules, there was some justification for writing the kinetic energy of an electron as $R\theta$, but in the present theory in which the electrons are regarded as moving under the influence of the forces of the di-poles, the assumption is clearly highly arbitrary. The prediction of the Wiedemann-Franz ratio also depends on the assumption that the di-poles consist of charges $+e$ and $-e$ separated by a distance comparable with that between two atoms, and although possibly justifiable at the time the theory was first introduced, this assumption is now entirely contrary to the evidence, particularly since the theory assumes that the loosely bound or free electrons are not those which give rise to the di-poles. In the case of the atom of a metal such as sodium, for example, if the one loosely bound valency electron were concerned in the formation of the di-pole, we might possibly consider a degree of polarity of $+e$ and $-e$ at a distance comparable with that between the atoms. But this is just what the di-pole theory does not do. It supposes rather that the free or loosely bound valency electrons are passed on from one di-pole to another, so that the di-poles themselves are the sodium ions, and the whole of the evidence from compressibility and other subjects

indicates that such a marked degree of polarization is most improbable. For these and other reasons the theory has now been discarded, although in its time it was a most ingenious attempt to cover the supra-conductivity and other electrical properties.

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2. The Theory of Wien and Grüneisen

The theory of Wien and Grüneisen occupies a very curious and interesting position, for on the one hand it involved several completely new conceptions, some of which are now generally accepted as being true, whilst, on the other hand, it supported these ideas by showing an apparent agreement between fact and theory which later work has shown to be unjustified, and in connexion with which later criticism has thrown much doubt as to the validity of the methods of calculation used.

The theory begins by assuming that while the electrical conductivity of metals is due to the presence of free electrons moving between the atoms, the velocity of these electrons is independent of temperature, so that they make no contribution to the specific heat. Exactly the same line of reasoning is used as in the simple electron gas theory, so that the electrical conductivity is given

by a relation of the type $C = \frac{e^2 N \lambda}{2m v}$, but since both N and v are

assumed to be constant, the whole of the change in the electrical conductivity is thrown upon the mean free path λ , and the theory assumes that the length of the free path depends solely upon the amplitude of the atomic vibrations. It is here that the theory makes such a great advance upon the older views, for it is the first theory in which the atomic vibrations are treated quantitatively as determining the magnitude of the electrical conductivity. The picture presented is that the electrons move in guided paths between the atoms, and that, as the temperature rises, the atomic vibrations increase in amplitude, and so tend more and more to hinder the passage of the electrons. The marked decrease in the conductivity when a solid solution is formed is considered as due to the fact that the solute atom causes a distortion of the lattice, and so breaks up the long guided path between the atoms. This kind of explanation, which is now generally accepted, requires inevitably that the motions of the electrons are not haphazard as imagined by the simple 'electron

gas' theories, but are definitely related to the crystal structure, and it is here that the theory makes its chief advance.

The Wien theory does not explain the thermal conductivity, or the constancy of the Wiedemann-Franz ratio, and this disadvantage was recognized by Wien himself. The theory considers that when a metal is heated, the atoms acquire additional energy according to the ideas of the quantum theory, but that this additional energy cannot be transmitted to the electrons whose velocity remains constant. On the other hand, when the electrons drift under the action of an electric force, they are regarded as acquiring a small additional velocity in the direction of the force, and it is assumed that the additional energy so gained can be transferred to the atoms during the collisions, with the production of the Joule heating effect. The exact physical picture presented here is rather confusing, for we are naturally led to inquire why, during collisions between electrons and atoms, the atoms can gain energy from the electrons, when the reverse transference of energy cannot take place.

From quantum considerations Wien deduced relations between the conductivity and temperature which involved the characteristic frequencies of the atomic vibrations in the various metals, but a detailed comparison shows that the agreement between fact and theory is really not so good as Wien at first concluded from a comparatively few examples.

The theory of Wien was concerned solely with the effect of temperature upon the electrical conductivity, and it was owing to the work of Grüneisen that the theory was extended to explain the effect of hydrostatic pressure upon resistance. Grüneisen deduced that the effect of pressure would be to increase the frequency, and so to diminish the amplitude of the atomic vibrations, and hence that the resistance should diminish under pressure. From this point of view he obtained an expression giving the pressure coefficient of resistance in terms of quantities, most of which were known, and by means of various simplifying assumptions a fairly good agreement between fact and theory was obtained. As we shall see later, the methods of calculation are open to criticism, but the fact that a result of the right magnitude was obtained was in itself a considerable triumph.

The Effect of Temperature on Resistance (Wien).¹

In this theory, as previously stated, we adopt the same line of reasoning as in the simple electron gas theory, according to which

the specific conductivity is given by an expression of the type

$$C =$$

Since we assumed both N and λ to be constant, we may write, for the specific resistance W ,

$$W = \frac{1}{C} = A \frac{1}{\lambda}.$$

There is here some slight confusion about the meaning of the term N , for strictly speaking this should be the number of electrons per unit volume, whereas it is really meant to be assumed that the number of free electrons per atom, or per gram, remains constant. Actually therefore the term N should be a variable depending on the volume expansion of the metal, but, in dealing with the effect of temperature, this change produces a relatively unimportant effect, and we may therefore follow Wien, and treat N as being constant.

We have therefore to consider how the amplitude of the atomic vibrations will influence the mean free path of an electron, which is inversely proportional to the number of collisions which an electron makes in unit time. By applying the older quantum theory, it can be shown that there is only one relation between the number of collisions and the amplitude of the atomic vibrations which makes the number of collisions per unit time independent of the exact distribution of energy among the atoms. This condition is that the number of collisions shall vary as the square of the amplitude. Subject to this assumption Wien deduces that the specific resistance will be given by

$$W = B \left(\frac{\theta}{\beta} \right)^2 \int_0^{\rho_m} \frac{\rho d\rho}{e^{\rho} - 1}, \text{ where } \rho = \frac{\beta\nu}{\theta},$$

and ν_m is the limiting frequency so that $\rho_m = \frac{\beta\nu_m}{\theta}$, where $\beta = \frac{h}{k}$ (h is Planck's constant, and k the Boltzmann constant). This is the equation representing the effect of temperature upon resistance, and the solutions are different for high and low temperatures. These two solutions are as follows:

1. *At Normal and High Temperatures* where $\frac{\beta\nu_m}{\theta}$ is small,

$$W_{\theta} = B \frac{\theta\nu_m}{\beta} \left\{ 1 - \frac{1}{4} \frac{\beta\nu_m}{\theta} + \frac{1}{36} \left(\frac{\beta\nu_m}{\theta} \right)^2 - \frac{1}{3600} \left(\frac{\beta\nu_m}{\theta} \right)^4 \dots \right\} \quad (1)$$

so that at a sufficiently high temperature the resistance varies with the temperature according to a relation of the type $a(\theta - b)$, which is in agreement with fact.

2. *At Low Temperatures* where $\frac{\beta\nu_m}{\theta}$ is no longer small the expression for the resistance reduces to

$$W = B \left(\frac{\theta}{\beta} \right)^2 \int_0^{\rho_m} \rho d\rho \{ e^{-\rho} + e^{-2\rho} + e^{-3\rho} \dots \}$$

and at very low temperatures this reduces to

$$W = B \left(\frac{\theta}{\beta} \right)^2 \frac{\pi^2}{6} \dots \dots \dots (2)$$

so that the temperature coefficient of resistance should vanish at the absolute zero which is generally the case where supraconductivity is not shown.

The validity of equation (1) may be tested by comparing the predicted and observed values of the temperature coefficient of resistance, for it can be seen that as long as $\frac{\beta\nu_m}{\theta}$ is small, we have

$$\begin{aligned} \frac{W_\theta}{W_{273}} &= \frac{\theta}{273} \left[\frac{1 - \frac{1}{4} \left(\frac{\beta\nu_m}{\theta} \right) + \frac{1}{36} \left(\frac{\beta\nu_m}{\theta} \right)^2 \dots}{1 - \frac{1}{4} \left(\frac{\beta\nu_m}{273} \right) + \frac{1}{36} \left(\frac{\beta\nu_m}{273} \right)^2 \dots} \right] \\ &= \theta \left(0.00366 + \frac{\beta\nu_m}{298000} \right) - \frac{1}{4} \frac{\beta\nu_m}{273} \text{ approximately.} \end{aligned}$$

The temperature coefficient should therefore be somewhat greater than 0.00366 in agreement with fact, and it should be greater for those metals with high characteristic frequencies, i.e. large values of $\beta\nu_m$. In agreement with this prediction Wien pointed out that iron and nickel, with high characteristic frequencies, also had high temperature coefficients, but, as shown by Bridgman at the Solvay Congress in 1924, when the list is extended to cover a large number of metals, all correspondence between the temperature coefficient and characteristic frequency appears to vanish. The theory does, however, give the right magnitude for the temperature coefficient except at very low temperatures, where the quantitative side of the theory begins to break down.

In the above simple derivation of the theory Wien used the earlier quantum theory according to which the mean energy content of an atom depends solely on the temperature, and is

given by an expression of the type $U = \frac{h\nu}{e^{\hbar\theta} - 1}$. Application

of the later theories involving the conception of zero-point energy ('Nullpunktenergie') remaining at the absolute zero of temperature, led to little but speculation, although they involve considerable differences in the equations at very low temperatures. At normal or high temperatures the results are, however, but little affected.

The Effect of Pressure on Resistance (Grüneisen).²

We have already noted (p. 17) Grüneisen's discovery that at low or moderate temperatures the resistance of a metal varies approximately as the product of the atomic heat and the absolute temperature, so that $\frac{W}{\theta} \propto C_p$. This relation is purely empirical,

and is not in agreement with the simple Wien theory, and Grüneisen considered various possibilities, including the suggestion of Wien that the electron velocity v might be connected with the characteristic frequency by a relation of the type $\frac{1}{2}mv^2 = h\nu$. In each case, however, little but speculation resulted, but in spite of this Grüneisen extended Wien's theory, and obtained what was described as a more generalized expression connecting the mean free path and the temperature, this expression being

$$\frac{1}{\lambda} = D \frac{k}{M\nu_m V} f\left(\frac{\theta}{\beta\nu_m}\right) \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (3)$$

where M and V are the atomic weight and atomic volume respectively. The new point here is the introduction of the atomic volume V , and unfortunately no account is given as to how this equation is derived, although according to Bridgman the term V may contribute as much as 25% of the total effect.

This is, however, the expression used in Grüneisen's work on the effect of pressure on resistance, the expressions for which are deduced as follows.

According to the Quantum Theories of the solid state developed by Grüneisen and others, the entropy, S , of a monatomic element at not too high temperatures is, to an approximation, a function only of $\theta/\beta\nu_m$. Hence under isentropic or adiabatic compression any function of $\theta/\beta\nu_m$ must remain constant. Consequently in the generalized equation (3) given above, the f term must remain constant for adiabatic compression, and we have

$$-\frac{1}{\lambda} \left(\frac{\partial \lambda}{\partial p} \right)_S = -\frac{1}{\nu_m} \left(\frac{\partial \nu_m}{\partial p} \right)_S - \frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_S \quad \cdot \quad \cdot \quad \cdot \quad (4)$$

In the general development of the theory of the solid state which resulted from the conception of fundamental atomic frequencies, it was shown by Grüneisen (3) that, under adiabatic compression, the characteristic frequency was given by the relation

$$\frac{1}{v_m} \left(\frac{\partial v_m}{\partial p} \right)_s = \frac{1}{\theta} \left(\frac{\partial \theta}{\partial p} \right)_s = \frac{1}{C_p} \left(\frac{\partial V}{\partial \theta} \right)_p \quad (5)$$

so that if κ_s be the adiabatic compressibility

$$-\frac{1}{\lambda} \left(\frac{\partial \lambda}{\partial p} \right)_s = -\frac{1}{C_p} \left(\frac{\partial V}{\partial \theta} \right)_p + \kappa_s \quad (6)$$

In absolute measure κ_s is about one-half of the term $\frac{1}{C_p} \left(\frac{\partial V}{\partial \theta} \right)_p$, so that the free path λ should increase under adiabatic compression, and hence *a fortiori* λ should increase under isothermal compression, for adiabatic compression means a rise of temperature with consequent shortening of λ if the Wien theory be correct.

Hence using the general rule

$$\left(\frac{\partial}{\partial p} \right)_s = \left(\frac{\partial}{\partial p} \right)_\theta + \left(\frac{\partial}{\partial \theta} \right)_p \left(\frac{\partial \theta}{\partial p} \right)_s$$

and using $\alpha = \frac{1}{W} \left(\frac{\partial W}{\partial \theta} \right)_p$ for the temperature coefficient of resistance, we have

$$\frac{1}{W} \left(\frac{\partial W}{\partial p} \right)_\theta = \frac{1}{W} \left(\frac{\partial W}{\partial p} \right)_s - \alpha \left(\frac{\partial \theta}{\partial p} \right)_s$$

consequently since $W \propto \frac{1}{\lambda}$, we have from (5) and (6) and the

fundamental equation $W = \frac{2mv}{e^2 N \lambda}$

$$\frac{1}{W} \left(\frac{\partial W}{\partial p} \right)_\theta = \frac{1}{v} \left(\frac{\partial v}{\partial p} \right)_s - \frac{1}{N} \left(\frac{\partial N}{\partial p} \right)_s + \kappa_s - \frac{1}{C_p} \left(\frac{\partial V}{\partial \theta} \right)_p [1 + \alpha_\theta \theta]. \quad (7)$$

This is the general equation connecting pressure and electrical resistance, and it is then simplified by making the following approximations.

In general agreement with the views of Wien that the velocity of the electrons is constant, the Grüneisen theory assumes that the term $\frac{1}{v} \left(\frac{\partial v}{\partial p} \right)_s$ can be neglected.

It was further assumed by Grüneisen that the term $\frac{1}{N} \left(\frac{\partial N}{\partial p} \right)_s$

could also be neglected in accordance with the general views of Wien that N is little affected by external conditions, and this was regarded as confirmed by the work of Wagner⁴ on the effect of pressure on thermo-electric properties. As we shall see later, this assumption is open to serious objections.

Subject to the above assumptions, however, the equation for the pressure coefficient reduces to

$$\frac{1}{W} \left(\frac{\partial W}{\partial p} \right)_{\theta} = \kappa_s - \frac{1}{C_p} \left(\frac{\partial V}{\partial \theta} \right)_p [1 + \alpha_{\theta} \theta] \quad . \quad . \quad . \quad (8)$$

and since the first term is less than the second, the resistance should diminish under pressure in agreement with fact.

For a limited number of metals Grüneisen found a remarkably good agreement between the calculated and observed values for the pressure coefficients of resistance, except for one or two metals of low melting-point. In later papers Beckman⁵, and Bridgman⁶, have extended the comparison to a large number of metals, and the right order of magnitude is found to be given in nearly every case, although more than this cannot be said.

Discussion.

The real advance made in the Wien-Grüneisen theory is that, for the first time, the effect of the atomic vibrations upon the length of the free path is taken into account quantitatively. At all except the lowest temperatures the theory gives the right order of magnitude for the temperature coefficient of resistance, although the exact correspondence between these coefficients and the atomic frequencies, which the Wien theory requires, is not fulfilled, which indicates that the details of the calculations are incorrect.

The theory has been criticized on the grounds that it does not agree with supra-conductivity, and if the electrons are conceived of as small bullets moving along rows of massive spherical atoms, it does indeed appear difficult to understand supra-conductivity in polycrystalline metal, where the motion of the electron must change direction in passing from one crystal to another. But it is doubtful whether we are justified in arguing in this way, for, in the first place, the motion of an electron down a guided path is not that of one small neutral particle among larger ones, but is much more that of an electrified particle in a periodic field, whilst, apart from this the fields of force round the atoms or ions may themselves be fluctuating owing to the motions of the

electrons which remain bound to the atoms, and if these fluctuations are in phase, as they may be at low temperatures, they may serve to pass the electrons on from one atom to another and so give rise to supra-conductivity. This criticism of the Wien theory is therefore unjustified until much more is known of the conditions of motion of the electrons, and of their interaction with the ions, and it is of course becoming increasingly apparent that the old simple picture of bullet-like electrons colliding with spherical atoms is incomplete, and in some ways misleading.

The general ideas of Grüneisen have been criticized by Bridgman on the ground that the theory ignores the effect of pressure upon the volume, for although the effect of pressure upon the inter-atomic distances is relatively 5 to 10 times less than its effect on the amplitudes of the vibrations, the absolute magnitude of the latter is only about $\frac{1}{20}$ th of the inter-atomic distance, so that on the whole, the size of the channels down which the electrons pass should diminish under pressure even if the atoms are considered as points, and *a fortiori* when they occupy a definite volume. Here again the criticism appears unjustified unless we make definite assumptions about the zones of repulsion surrounding the atoms or ions, for if these are continually oscillating the important thing may not be the distance between the atoms, but the extent to which the oscillations of the repulsive zones are thrown out of phase by the thermal vibrations, and in this case the general ideas of Grüneisen may be correct.

The quantitative methods of Grüneisen have, however, been seriously criticized by Bridgman. Apart from the unsatisfactory nature of the 'generalized' equation on p. 214, the simplification of the fundamental equation (7) is open to criticism. We have already noticed that strictly speaking the term N representing the number of electrons per unit volume is not constant but varies with the volume, since the real assumption is that the number of electrons per atom is constant, in which case not N , but NV will be constant. Actually Grüneisen assumes neither one thing nor the other, but leaves N in the equation, and then differentiates it, and assumes that the term $\frac{1}{N} \left(\frac{\partial N}{\partial p} \right)_s$ can be neglected, which is considered justified from the results of Wagner on the effect of pressure on thermo-electric properties. Wagner's conclusions were, however, based on the old electron gas theories which are in contradiction to the present theory, but apart from this point it seems clear that if the real assumption is that NV

is constant, then if the term $\frac{1}{N} \left(\frac{\partial N}{\partial p} \right)_s$ is to be neglected, the compressibility term κ_s in equation should also be omitted, in which case the numerical values may be affected by 25% or more. The apparently almost exact agreement between the experimental results and those calculated by Grüneisen's equation is thus largely the result of leaving out terms in a very arbitrary manner, although the fact that the right order of magnitude is obtained is a distinct achievement.

The Wien-Grüneisen theory is thus of great interest as leading away from the simple 'gas' conception, and introducing the effects of the atomic vibrations. It was unsatisfactory in that it ignored the thermal conductivity entirely, since the assumption of an electron velocity independent of temperature made it impossible to account for the conduction of heat by electrons. In many ways, however, the theory is really a rough forecast of the more recent theories of Sommerfeld, Houston, and Bloch (Chapter XIII), and in these the difficulty in connexion with the thermal conductivity is avoided.

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3. Grüneisen. *Ann. Phys.* 1912, 39, 276.
4. Wagner. *Ann. Phys.* 1903, 27, 955.
5. Beckman. *Ann. Phys.* 1915, 46, 481, 931; *Phys. Z.*, 1915, 16, 59.
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3. The Theory of Bridgman

General.

This theory was put forward by Bridgman in a series of papers beginning in 1917, and developed simultaneously with the same worker's experiments on the effect of pressure on the electrical properties of metals. The essential fact with which the author was concerned was that in nearly all cases the electrical resistance of a metal decreases under hydrostatic pressure, whereas the older electron theories led one to expect an increase. This difficulty was overcome by the comparatively simple assumption that electric conduction takes place, not by the movement of the electrons between the atoms, but by a motion in some kind of guided path or quantized orbit through the substance of the atom itself. At very low temperatures the electrons are regarded as passing perfectly freely from one atom to another, so that

supra-conductivity is met with. But, as the temperature rises, the amplitude of the atomic vibrations increases until a point is reached where, at intervals, adjacent atoms are so widely separated that an electron can no longer pass freely from one atom to the other, and in this way the resistance is created. We may express this crudely by saying that at low temperatures the atoms are in contact, but that, as the temperature is raised, gaps begin to appear between them, but this, of course, is not to be taken as implying that the gaps occupy fixed places in the solid metal. A gap may be said to be formed when the distance between two adjacent atoms exceeds a certain critical value, and although the positions of such gaps are continually changing, their average number per unit volume at any instant will be constant under given conditions, and statistically we may assume that there are so many atoms in contact and so many gaps.

If the amplitudes of the atomic vibrations are distributed over a wide range we shall not expect supra-conductivity to appear suddenly as the temperature is lowered, but if, on the other hand, the amplitudes vary discontinuously, or are closely clustered round a mean value, there will be a definite temperature at which a finite number of gaps will suddenly vanish, and supra-conductivity may be expected to appear sharply.

According to this theory the effect of pressure is in the first place to bring the atoms into closer contact, and so to facilitate the passage of the electrons from one atom to the next. But, apart from this, increase of pressure diminishes the amplitude of the atomic vibrations, and so reduces the chance that two adjacent atoms become so far separated as to form a gap.

In the earlier developments of the theory the number of conducting electrons was not considered. It was found that the change of resistance with temperature, pressure, &c., was approximately twice the relative change in the amplitude of the atomic vibrations, and in this way, from fundamental thermodynamic considerations, equations were deduced connecting the pressure and temperature coefficients of resistance with the corresponding coefficients for the effect of pressure and temperature upon the amplitudes and the volume. These equations were quite independent of the number of electrons concerned in the conduction, and at this stage the theory ignored the thermal phenomena, but in order to cover these the following additional assumptions were made.

It was assumed that the number of conducting electrons is con-

stant but very small compared with that of the atoms, and that the electrons move with the velocities required by the older equipartition theory. The mechanism involved is that the electrons move through the atoms with the velocities required by the older free electron theories, and the gaps between the atoms give rise to the resistance in much the same way as the collisions in the older theories. In fact, to use a very crude phrase, the electrons move through the atoms with the velocities required by the kinetic theory, and then collide with the gaps. In this way the expressions for the conductivities are the same as those of the older theories, but a much longer free path is possible, since a gap does not necessarily occur between every two atoms, for there may be many atoms in contact in a row before a gap is met with.

In the original Bridgman theory the expression for the Wiedemann-Franz ratio was the same as that given by the older electron-gas theory, but, after discovering that the ratio varied under pressure, it was assumed that a considerable fraction of the thermal conductivity was non-metallic, or atomic, as distinct from electronic. This was regarded as confirmed by the fact that the observed Wiedemann-Franz ratios are greater than those given by the electron gas theories. From his work on the effect of pressure, Bridgman concluded that in some cases as much as one-third or one-half of the total conductivity may be atomic, and consequently the effect of pressure upon thermal conductivity becomes complex. The general picture presented is that the heat is carried by elastic waves down the rows of atoms which are in contact, but that, when a gap is reached, the last atom flies across the gap, and strikes the head of the next row, the impulse travelling down the row as an elastic wave until it reaches the end of the row, when the last atom may again fly off—much as an impulse travels down a row of billiard balls. The free path for atomic heat transfer is thus the same as that for electrical conduction, and the atomic heat conductivity will depend on the number of atomic heat transfers per unit time across unit cross-section of the metal, and this will involve the crystal structure, the closeness of the fit between neighbouring atoms, and other factors which cannot be determined. The maximum number of atomic heat transfers of energy per second down each string of atoms cannot, however, exceed ν , the frequency of the atomic vibrations, and by comparing the known values for the Wiedemann-Franz ratios with the maximum calculated atomic

thermal conductivities Bridgman was able to show that the mechanism postulated in his theory would require the number of atoms in the metal to be at least 10 to 30 times the numbers of free electrons for the more common metals. This was considered to confirm the general assumption that the number of electrons is small compared with that of the atoms, although, as we shall see later, this assumption involves many difficulties.

The Bridgman theory is the first in which any attempt is made to account for the effect of tension on the conductivity of metals, and these phenomena have been discussed at great length by Bridgman. The theory requires the resistance of normal metals to increase in the direction of stress, firstly because the distance between the atoms increases in this direction, and, secondly, because the amplitude of the vibrations in the direction of the tension will increase, in order to compensate for the decrease in period caused by the weakening of the restoring force on the atoms resulting from their increased distance apart. Conversely, the resistance at right angles to the direction of tension should diminish, but the exceptions can only be accounted for by assuming abnormal laws of force in the metals concerned, and the conception of considerable atomic thermal conductivity has again to be made in order to account for the variation of the Wiedemann-Franz ratio under tension.

In general it may be said that the detailed discussion of these points showed clearly that the older free electron theories are untenable, and that the electrons are probably best considered as moving in some kind of guided paths. But apart from this no satisfactory theory can be given, and it seems unlikely that further progress will be made in this direction until more is known of the effect of tension upon the conductivities of single crystals within the elastic limit.

Discussion.

The Bridgman theory thus covers a wide range of facts, but when examined in detail the assumptions involved appear in many cases to be mutually inconsistent, and improbable. The underlying assumption that the electrons move through the atoms, and not between them, may well be justified, for apart from the evidence that electrons can penetrate the outer shells of electrons surrounding an atom, the conception of shared electrons, which is supported by so much chemical evidence, is in many ways similar to the passage of electrons through the atoms

in some kind of quantized orbit as imagined by the Bridgman theory. But the assumption that the velocities of electrons moving in this way will vary continuously with the temperature so as to have the equi-partition value appears unjustified, for if the electron does move through the atom in a quantized orbit with no resistance, it is hardly likely that its velocity will vary in such a simple way.

The second assumption that the number of free electrons is small compared with that of the atoms, but constant, also appears improbable, since it implies that the atoms are not all in the same condition, so that there will be an equilibrium between ionized and non-ionized atoms, and we shall expect the number of free electrons to be given by a relation of the type $n = n_0 e^{-Q/R\theta}$. Unless Q , the heat of ionization, has an absurdly large value, this must imply a variation of n with θ , which is contrary to the assumption of a constant value for n , and even though the Bridgman theory does allow a much longer free path than the older theories, the conclusion seems inevitable that the conductivity should diminish at low temperatures.

The further assumption that such a large part of the thermal conductivity at ordinary temperatures is due to the atoms is also distinctly questionable. It is in direct contradiction to the conclusion of Grüneisen and Eucken (p. 77), who, from the analysis of their results for the thermal and electrical conductivities, concluded that the non-metallic, or atomic part of the thermal conductivity was important only at the lower temperatures. The assumption also makes it difficult to see why the thermal conductivity should be almost independent of temperature, and naturally leads us to inquire why the thermal conductivity of salts should be small when their constituent ions are closer together than the atoms in a metal.

For these and other reasons it is improbable that the details of the Bridgman theory are correct, but in other ways it may contain an indication of the truth. For, considered qualitatively, the real essence of the theory is that the motions of the electrons are not haphazard like those of gas molecules, but are intimately connected with the structure of the atoms, since this is what is implied when we speak of the electrons as passing through the atoms in some kind of a quantized orbit. While, therefore, apart from the general thermo-dynamic arguments, the details of the theory are almost certainly wrong, the general idea may in reality be one way of expressing the truth.

REFERENCES

A general account of the Bridgman theory is given in the Solvay Congress Report, 1924, pp. 96-112. The original papers are as follows:

Physical Review, 1917, 9, 269. General discussion with special reference to the pressure effect.

Ibid. 1921, 17, 161.

Ibid. 1922, 19, 114. Thermal conductivity, and tension effect.

Proc. Amer. Acad. Arts Sci. 1923, 59, 119. Effect of tension.

4. The Dual Theory of E. H. Hall

The Dual Theory of Metallic Conduction was put forward by E. H. Hall in 1917-18, and has since been extended in a long series of papers to which reference will be found on page 229. Like the other theories of its time, it was at first an attempt to overcome the difficulty in connexion with the specific heats which was encountered by the older electron gas theories. But the assumptions of the Dual Theory were later found to give a qualitative explanation of thermal conductivity, and the theory was then extended so as to deal with the electro-magnetic and thermo-magnetic properties, and also with the emission phenomena. Many of the difficulties which the theory was devised to meet have since been overcome more satisfactorily by other means, and for this reason we shall only give a general outline of the methods employed.

The fundamental assumption of the Dual Theory is that the electrons taking part in electric conduction can be divided into two classes—a comparatively small number of free electrons which obey the simple gas laws, so that their kinetic energy varies directly as the absolute temperature, and a much larger number of associated electrons of which the energy does not vary with the temperature. The free electrons are regarded as those concerned in thermionic emission, whilst the associated electrons are bound to the atoms, but the bond is of such a nature that they may pass freely from one atom to another, and so serve to carry the electric current. In this way the difficulty in connexion with the specific heats is avoided, since only the small number of free electrons contribute to the heat capacity. For convenience we shall denote the constants referring to the free and associated electrons by the suffixes *F* and *A* respectively—thus C_F means the conductivity due to the free electrons, and C_A that of the associated electrons.

The theory assumes that in every part of a metal there is an

equilibrium between the neutral atoms and the positive ions, and that this equilibrium obeys the ordinary laws of mass action. We may now consider, from this point of view, what will happen when one end of a bar of metal is heated. Since the free electrons obey the gas laws, the pressure will rise in the hot part of the metal, and they will tend to flow towards the colder parts. But this accumulation of electrons in the cold part will upset the equilibrium of the reaction $\text{atom} \rightleftharpoons \text{ion} + \text{electron}$, and consequently some of the free electrons at the cold end will recombine with atoms, with *evolution* of heat. Similarly the flowing away of electrons from the hot end of the bar results in the dissociation of atoms with *absorption* of heat at the hot end. From this point of view an unequally heated piece of metal contains a continual stream of free electrons from hot to cold, and of associated electrons in the opposite direction, and the thermal conductivity is due partly to the free electrons according to the principles of the Drude-Lorentz theories, and partly owing to the continual process of ionization with heat absorption at the hot end of the bar, and of re-association with heat evolution at the cold end. This explanation does not, however, account for the Wiedemann-Franz Law.

In order to proceed further we have to consider what is likely to affect the motion of the associated electrons, and the theory assumes that this is decided largely by the action of the comparatively few positive ions from which the free electrons are formed. The underlying picture is that a positive ion, since it has lost an electron, has a 'gap', a 'vacancy', in its electronic structure, and that if this gap comes into suitable proximity to a neighbouring neutral atom, an associated electron may fly across from the neutral atom, which thereby becomes an ion, to the ion which is changed into a neutral atom. This part of the theory was originally accompanied by some very speculative suggestions that the neutral atom was spherically symmetrical, but that the ions were markedly unsymmetrical and polarized. In many cases this is, however, undoubtedly incorrect. Thus in the case of metals such as the alkalis or copper, silver, and gold, it is certainly the underlying ion, with the completed group of electrons, which is symmetrical, and the neutral atom which is liable to polarization.

At first it might be thought that the process imagined to take place during thermal conduction would also occur when two different metals were in contact. For if the free electrons in the

two metals had different pressures they would flow from one metal to another, and this would upset the equilibrium (atom \rightleftharpoons ion+electron) and therefore cause a flow of associated electrons in the opposite direction. This, however, would result in a transference of heat without an initial difference of temperature, and, since this is contrary to the principles of thermo-dynamics, it is assumed that it is prevented by the differences in the attractions of the ions in the two metals. If the ratios of the conductivities of the free and associated electrons are different in two metals a stream of electrons crossing a boundary will cause ionization on one side and re-association on the other, and since these processes involve heat absorption and evolution they are intimately connected with the Peltier Heat. The theory also gives an account of the different effects of pressure upon resistance in different metals. As in the older theories the conductivity, C_F , of the free electrons should decrease with pressure, but the conductivity of the associated electrons, C_A , should increase, because the atoms are brought closer together. Consequently for small values of $\frac{C_F}{C_A}$ we should expect the conductivity to increase under pressure, whilst the conductivity should decrease for large values of $\frac{C_F}{C_A}$. In the original paper it was assumed that in metals such as bismuth where the total conductivity was small, the value of $\frac{C_F}{C_A}$ was large, i.e. the associated electrons were strongly bound and contributed but little to the conductivity. In support of this it was pointed out that bismuth and antimony with low conductivities showed a decrease in conductivity under pressure, but the later work of Bridgman (p. 20) shows that lithium, caesium, barium, and strontium all behave abnormally under pressure, so that the explanation is probably much more complex.

The theory also offers a very ingenious explanation of the thermo-magnetic and galvano-magnetic phenomena, the author being, of course, the discoverer of the well-known Hall Effect. In the original simple developments of the theory it was assumed, as in the Drude-Lorentz theories, that the free electrons were acted on by the magnetic field so as to give a negative Hall Effect. It was further concluded that the associated electrons also gave rise to a Hall Effect, whose magnitude might be greater or smaller than that due to the free electrons. The picture presented is therefore that a stream of free electrons moves in one

direction, and of associated electrons in the other, and the resultant sign of the Hall Effect depends upon which is the greater. The position is similar to that of two cells of different E.M.F. joined in opposition as shown in Fig. 47, where a cyclic

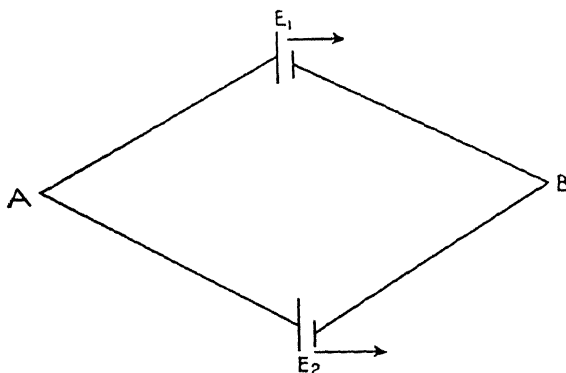


FIG. 47.

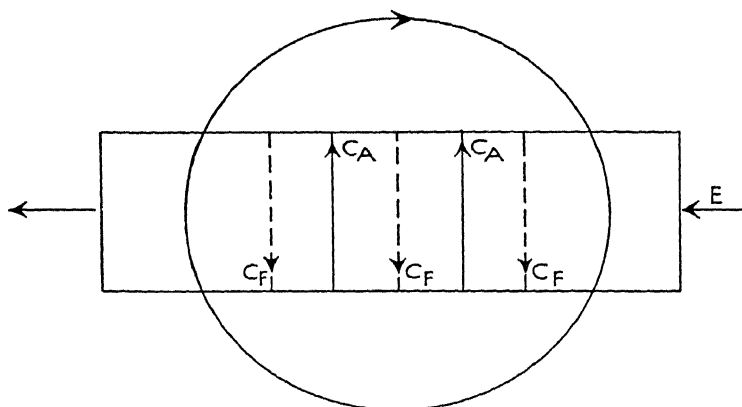


FIG. 48.

current flows clockwise if $E_1 > E_2$, and counter clockwise if $E_2 > E_1$, the potential of point A being less than that of B in each case.

Similarly in the plate imagined for the Hall Effect in Fig. 48, the free electron stream crosses the plate in one direction, and the associated electron stream in the other, and the direction of

the net Hall effect depends upon the relative magnitudes of the two. Further since ionization and re-association involve heat absorption and evolution we understand why the Ettinghausen and Righi-Leduc effects are produced, and why these may have different signs. In a later paper (12) the matter was examined more closely, and the conclusion was reached that it was really very much more complex, and that the interaction of the atoms had to be taken into account.

So far we have dealt with the theory from the qualitative point of view only, but numerous attempts have been made to develop it quantitatively. In order to do this it is necessary to make several quite arbitrary assumptions, of which the chief are as follows:

(1) It is assumed that over a small temperature range, the number of free electrons is related to the temperature by the equation

$$n = z\theta^q$$

where θ is the absolute temperature, and z and q are constants, of which for many purposes z need not be known.

(2) The ratio of free electron conductivity C_F , to total conductivity C , is assumed to be

$$C_F/C = K + K_1 t + K_2 t^2$$

where t is the temperature in degrees centigrade, and K_1, K_2, K_3 are constants.

(3) The heat of ionization within a metal is assumed to be given by

$$H = H_0 + sR\theta$$

where R is the gas constant, and s and H_0 are constants of the metal.

In this way each metal has seven characteristic constants z, q, K, K_1, K_2, H_0 , and S , and much ingenuity was shown in trying to select the most probable values of these in order that the equations deduced for the various effects should agree with the facts. These arguments are, however, not always very convincing, for they involve the assumption that by omitting one term, an expression deduced for the Thomson Heat can be identified with a purely empirical relation found by Bridgman, whilst in many cases the equations are approximations only, and methods of trial and error are used in order to select the constants. We may note, however, that the expression deduced for the Peltier

Effect involves the term C_F/C , and since the values of this ratio are not necessarily the same in different directions in a crystal, the internal Peltier Heat can be accounted for.

The Dual Theory is thus extremely ingenious and can be made to cover a large number of facts in a qualitative way. It has received comparatively little attention owing to the unsatisfactory nature of its quantitative developments, which are undoubtedly open to criticism. The mere fact that the theory is complex is by no means a condemnation, for it is increasingly apparent that the problems of conductivity, thermo-electricity, &c., are of a very complex nature. But the introduction of so many constants which can neither be determined theoretically, nor by direct comparison with experiment, is an almost fatal weakness of the theory in its present form. In many places the equations are admittedly of an approximate nature only, so that methods of trial and error, or arbitrary selection have to be made, and it becomes increasingly difficult to see how much of the apparent agreement is really due to the theory, and how much to a purely arbitrary selection of constants.

The fundamental assumptions of the theory are, however, in many ways most curiously interesting. As we shall see later, the evidence of the crystal structures of the metals indicates clearly that in the borderline metals such as silicon, antimony, bismuth, and tellurium, the atoms are bound together by forces of the same nature as those in the co-valent bonds of chemistry—i.e. by electrons shared between two atoms. In such cases the conductivity is probably the result of the gradual breakdown of the co-valent bond as the temperature is raised, and the distinction between free and bound electrons may well exist as postulated in the dual theory. But whether in this case there is an interchange between, or a conductivity due to the bound electrons is much less certain. Apart from this, as we shall see later, the theories based on the new quantum mechanics do in fact indicate that the velocities of the free electrons are distributed in such a way that the velocities vary from zero to a certain critical value, which is exceeded by a comparatively few electrons, and that it is these few electrons which are primarily concerned in emission and similar phenomena, although there is no sharp distinction between these electrons and the remainder. The postulates of the Dual Theory did thus contain an element of truth, although the quantitative developments and the detailed mechanical pictures are almost certainly incorrect.

REFERENCES

The chief papers dealing with this theory are all by E. H. Hall, and are as follows:

General

1. *Proc. Amer. Acad. Arts Sci.* 1914, 50, 68.
2. *Proc. Nat. Acad. Sci.* 1918, 4, 98; corrections to this paper on p. 297.
3. *Ibid.* 1920, 6, 139, 613.
4. *Ibid.* 1921, 7, 98, 62.
5. *Ibid.* 1922, 8, 307.
6. *Ibid.* 1926, 12, 327, 486.
7. *Ibid.* 1927, 13, 43, 315.
8. *Ibid.* 1928, 14, 377.
9. *Physical Review*, 1926, 28, 393. A general account.

Thermo-Magnetic, and Galvano-Magnetic Effects

10. *Proc. Nat. Acad. Sci.* 1923, 9, 41.
11. *Ibid.* 1925, 11, 416.
12. *Solway Congress Report*, 1924, p. 303.

XII

THE ELECTRON LATTICE THEORY OF LINDEMANN

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1. General

THE Electron Lattice theory was first put forward by Lindemann¹ in 1915, and was again discussed at the Solvay Congress² in 1924, and by Hume-Rothery in 1927 in a paper in the *Philosophical Magazine*.³ Somewhat modified forms of the theory have also been put forward by J. J. Thomson,⁴ and by Borelius,⁵ whilst the underlying conceptions have been discussed by many workers in connexion with the crystal structures and compressibilities of the metallic elements.

The theory involves a complete departure from all the 'free' electron theories, in that it considers the electrons, in the absence of a current, not to be moving about through or between the atoms, but rather to be situated on a space lattice interpenetrating the atomic lattice. From this point of view we are to look upon the crystal of a metal as built up of two interpenetrating lattices, one of electrons, and the other of atoms. When once this fundamental conception has been grasped, it is necessary to make two further assumptions in order to cover the facts.

(1) It is assumed that although attracted by the ions at distances greater than the atom's radius, the electrons are repelled at distances less than a critical value r_0 , by a force which may be put equal to $kf(r)$ where f is an unknown function. This hypothesis is in reality involved in almost all of the older theories in which the electrons are regarded as colliding with the atoms, for if the electron were simply attracted by a force e^2/r^2 this would become continually greater as the electron approached the atom or ion, and the small kinetic energy attributed to the electron, namely $a\theta$, would never enable it to remain dissociated. This assumption is therefore really contained in all the older theories although this was not expressly stated.

(2) The second assumption is that the number (N) of electrons per unit volume, the dielectric constant of the ions (D), and the constant k of the repulsive force $kf(r)$ are such that

where ϕ and ψ are functions which we shall define more fully later. This assumption is made to account for the Wiedemann-Franz law, and it is thus a purely *ad hoc* assumption, but unlike the assumptions made for the same purpose in some of the other theories, it does not seem to require anything which is inherently improbable.

Conduction of electricity through the metallic crystal is then considered to take place by the drifting of the electron lattice through the atomic lattice, the electrons passing in channels between the atoms, and their motion being interfered with by the atomic vibrations. In this respect the theory resembles that of Wien and Grüneisen, except that the electrons are no longer considered as moving independently down the channels, but are regarded as moving as one whole lattice.

In the original paper of Lindemann it was suggested that if the distance to which the repulsive force, r_0 , of the ions extends be less than $\frac{r}{2}$, half the distance between the centres of the atoms, the electron lattice will be able to move unimpeded through the atomic lattice as long as the amplitudes of the atomic vibrations are less than $\frac{r-2r_0}{2}$ and that this will correspond to the phenomenon of supra-conductivity. This explanation by itself is not, however, completely satisfactory, since, in the first place, it does not explain why supra-conductivity is shown only by a few metals which seem to have no very general characteristics of crystal structure, &c., distinguishing them from others, whilst, apart from this, the fact that supra-conductivity is shown by rings of polycrystalline metal seems to demand something more than a mere unimpeded passage of electrons along guided paths. It was suggested later by Hume-Rothery² that the precessional motion* of the orbits of the electrons bound to the metal ions may cause the repulsive zones surrounding the positive ions to fluctuate periodically, and that this fluctuation may help the passage of the electrons just as, to give a very crude mechanical picture, a number of marbles may be pushed along a plane by a series of revolving elliptical cams, if the latter are all exactly in phase. From this point of view, which we have already mentioned in connexion with the theory of Wien and Grüneisen, supra-conductivity may or may not occur according to the par-

* We are here using the terminology of the original Bohr theory. In the later theories the electronic orbits are no longer looked upon as flat disks.

ticular crystal structure, and the variation in the repulsive zones surrounding the ions. In support of this it is pointed out that in the B Group elements supra-conductivity is shown almost exclusively by those metals in which the crystal structures and inter-atomic distances indicate that the underlying ions have incomplete structures such as $(18)(2)^+$ in indium and thallium (see p. 326), since in these the repulsive zones may be expected to be less symmetrical in the crystal structure so that the fluctuation will be more marked.

As in the theory of Wien and Grüneisen, and the Di-pole theory of Thomson, the Lindemann theory regards the low conductivity of solid solutions as due to the destruction of the perfect regularity of the crystal lattice by the solute atom, and the same conception accounts for the absence of supra-conductivity. The pressure effect is again regarded as the result of the increase in frequency and decrease in amplitude of the atomic vibrations under pressure.

It is, however, when we come to the question of thermal conductivity that this theory makes its most novel suggestion, namely that the heat is conducted, not by the translational motion of the electrons, but by a series of elastic waves down the electron lattice, in the same way that, according to the Debye theory, heat is transferred in non-metallic crystals by a series of elastic waves. If a metal is composed of two interleaved space lattices, one of atoms and one of electrons, its thermal conductivity may be regarded as the sum of the conductivities due to the atomic space lattice, and that of the electrons. At ordinary temperatures the conductivity of the atomic space lattice will be of the same order of magnitude as that of a non-metallic crystal, and may therefore be neglected. On the other hand, as we shall explain later, calculation shows that as regards its thermal conductivity, an electron lattice, owing to the small mass of the electrons, will at room temperatures correspond to an atomic lattice at only one or two degrees above the absolute zero, and consequently its thermal conductivity will be very large. But the specific heat of such an electron lattice, which can be estimated by a formula due to Debye, can be shown to be negligibly small, and in this way a high heat conductivity can be accounted for without ascribing any measurable heat capacity to the electrons.

The remaining electrical properties are explained by the assumption that even though the electrons are situated on a space lattice within the metal, they will tend in many ways to

resemble a solution. Their mutual repulsion will be counter-balanced by the attraction of the positive ions, thus creating a condition analogous to the internal pressure of liquids in the theory of Van der Waals. The ease with which an electron is lost may be expected to increase with the atomic volume, and in this way we can understand why the metals with large atomic volumes (e.g. the alkalis) are electro-positive, and tend readily to lose electrons. In the same way the electrons will have a vapour pressure, and a general understanding of thermionic emission becomes possible.

The contact potential effects are explained much as in the older theories by assuming that the electrons tend to flow from a region of high to one of low internal pressure, and that, in so doing, a potential difference is created which eventually brings the process to a stop.

The thermo-electric effect is accounted for by the assumption that the internal pressures of the electrons do not vary in the same way with the temperature in different metals, so that a current is set up in a circuit of two metals with junctions at different temperatures. The Thomson Effect cannot, however, be evaluated, for while the electron lattice, as it moves through the atomic lattice, may be expected in some way to respond to the temperature variations of the latter, the exact relations involve a knowledge of the mechanism of interchange of energy between atoms and electrons which is largely unknown. The Hall Effect is explained as in the older electron gas theories since a magnetic field will affect the motion of the moving electron lattice, but the negative sign of the effect in some metals can only be explained, as in the older theories, by assuming that the external field affects the repulsive zones surrounding the ions. Since the thermal conductivity is regarded as due to elastic waves in the electron lattice, the thermo-magnetic effects are regarded as due to the deformation of the longitudinal elastic waves by the magnetic field with the production of a transverse electromotive force, but the problem cannot be attacked quantitatively. In all these spheres, therefore, the theory gives a general qualitative explanation of the facts, but quantitative methods are lacking, and it is in fact suggested frankly that when so little systematic knowledge exists in connexion with the electrical properties of metals, the time for detailed mathematical development has not yet arrived.

Apart from the electrical properties of metals, the conception

of an electron lattice has received much attention in connexion with the crystal structures, and compressibilities of the metals. The real starting-point of this work was the discovery by Hull⁶ that metallic calcium crystallized in the face-centred cubic structure, whilst in the structure of calcium fluoride, the calcium *ions* again occupied a face-centred cubic lattice, the fluorine ions being situated symmetrically inside the unit cube formed by the calcium ions. From this it was concluded by several investigators that in metallic calcium the structure was really essentially the same as that of calcium fluoride, a lattice of negatively charged valency electrons taking the place of the fluorine ions. The inter-atomic distances in the metal are, however, greater than those in the salts, but this is readily accounted for by the small size of the electrons. For in the salts, if we regard the oppositely charged ions as attracting one another, then since the ions are of comparable size, the closing together process is stopped by the 'contact'* of unlike ions, and equilibrium is reached when the direct electrostatic attractions between two ions is balanced by the repulsive forces due to the outer shells of electrons. But if an electron lattice exists in a metal, the electrons are so small compared with the atoms, that the closing together will be stopped by the contact between the similarly charged positive ions, and the equilibrium will be the result of a repulsion between the positive ions, and an attraction which is not directly between the ions, but is the result of the components of the pulls due to the electrons. In this way the differences in inter-atomic distances are readily accounted for, and we can also understand why so many of the metals crystallize in structures approximating to those of close-packed spheres, the electrons occupying the spaces in between the larger atoms. As pointed out by W. L. Bragg,⁷ this tendency is shown in the structures of many of the gem stones consisting of relatively large oxygen ions, and small metal ions, and we should therefore expect it to be shown if a metal consisted of interpenetrating lattices of electrons and atoms.

The bearing of an electron lattice upon compressibility has been discussed by Haber,⁸ Bridgman,⁹ and others, who have applied the theories of compressibility which were developed by Born in connexion with salts such as those of the alkali halides.

* The term 'contact' is here used for convenience, and is not meant to imply any sharp bounding surface. Two atoms or ions may be said to be in contact in a crystal at the distance at which the attractive forces are balanced by the repulsive forces.

In these the ions are regarded as bound together by electrostatic attractions varying inversely as the square of their distance apart, and the oppositely charged ions are drawn together until the attraction is balanced by a non-electrostatic repulsion due presumably to the fields of force produced by the shells of electrons. The general argument used by Born is to represent the potential of a unit cube by an expression of the type

$$\Phi = -\frac{a}{\delta} + \frac{b}{\delta^n}$$

where the first term refers to the electrostatic attraction, and the second to the repulsion which is assumed to vary as an inverse power of the distance. In the more elaborate extensions of the theory an additional term is introduced in order to allow for the polarization of the ions in each other's fields, but this is omitted here for the sake of simplicity.

In this equation the first term is definitely established for salts, the inverse square law for the electrostatic attraction having been proved experimentally by Born from measurements of dielectric capacity, and refractive index for long wavelengths, and by Slater¹⁰ from accurate compressibility data. The factor a can then be calculated for a series of point charges if the lattice type be known.

The second term, $\frac{b}{\delta^n}$, is, however, much less satisfactory, and is in reality a purely arbitrary assumption which has no real justification, except that, with large values of n , it gives a repulsion increasing rapidly at small distances in agreement with what is required. According to the accurate work of Slater the simple term $\frac{b}{\delta^n}$ is not in agreement with the facts if n is constant, and there is indeed little reason that it should be, although for small variations of δ it is a convenient approximation, since the expression readily gives values for $\frac{d\Phi}{d\delta}$ and $\frac{d^2\Phi}{d\delta^2}$. In the actual crystal, at the equilibrium distance, Φ will be a minimum, and hence $\frac{d\Phi}{d\delta} = 0$, so that $b = \frac{a}{n} \delta_0^{n-1}$ where δ_0 is the inter-atomic distance in the actual crystal. Further, since the pressure p , is given by $p = \frac{d\Phi}{dV}$ where V is volume, an expression can be obtained for the compressibility κ , and this is given by $\kappa = \frac{-9\delta_0^4}{(n-1)\alpha}$.

By comparing this with the observed values, it is found that $n = 9$ (approximately) for most of the alkali halides, except for the lithium salts for which $n = 5$. It must, however, be recognized that the values of n determined in this way are of a very arbitrary nature, since there is no real reason that the repulsion should be given by a term of the type $\frac{b}{\delta^n}$.

Bridgman and others have applied this theory to the compressibility of metals by assuming that an electron lattice replaces the negative ions, and in this way it is found that the application of the simple Born theory gives a value of the right dimensions for the compressibility. But any attempt to use a term of the nature $\frac{b}{\delta^n}$ for the repulsion leads to values of n very much smaller than those found for the corresponding salts. This, however, does not necessarily mean that the method is incorrect, for the inter-atomic distances in metals are much greater than those in salts, and there is little reason to suppose that the expression $\frac{b}{\delta^n}$ will give the repulsion over such a large range, although it may be a valid approximation for small variations in δ . For many of the metals the value of n is from 3 to 4, and criticism has been raised on the grounds that such low values of n are difficult to reconcile with electrons bound in a lattice, but indicate rather that the electrons are free. In order to meet this objection, the conception of a dynamic lattice was introduced by Haber, in which the electrons are considered to be on a lattice, but with the possibility of interchange from one point to another, so that while the probability of finding an electron in the neighbourhood of a point on the electron lattice is very much greater than that of finding one elsewhere, there is a continual interchange throughout the system. In view of the uncertainty of the $\frac{b}{\delta^n}$ term we shall not deal with the matter here, since compressibility is outside the scope of the present volume, but the subject is referred to because the electron lattice theory is one of the few theories which has received support apart from the purely electrical properties.

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2. The Electrical and Thermal Conductivities and the Specific Heats

In the electron lattice theory the number of conducting electrons is assumed to be constant, and the current strength will therefore be proportional to the mean velocity (u) of the electron space lattice through the metal. The mean velocity given to one electron by an external field X will be, as in the earlier theories, $\frac{eX}{2m}t$ where t is the time between two collisions. The value of t will, however, vary considerably according as the electron is very close to the atom, or at a much greater distance. If the electron be in the immediate vicinity of the atom, we may put $t = \frac{1}{\nu}$, where ν is the frequency of the atomic vibrations. For the remainder of the time, $t = \frac{d}{u}$ where d is the distance over which the electron is at a distance from the centre of the atom greater than $(r_0 + A)$, where A is the amplitude of the atomic vibration. In any measurable current there is always a large number of electrons within the distance $(r_0 + A)$, so that the time during which the entire electron lattice can move unimpeded will be infinitely short. Consequently since $u \propto X$, Ohm's Law may be expected to hold for any current whose duration is of the order $\frac{1}{\nu}$ or greater.

The exact variation of resistance (W) with temperature has not yet been calculated, but it will depend on the amplitude of the atomic vibrations, and on the law of force acting on the electrons when they are within the repulsive zones of the atoms, and since, according to the Debye and Born theories, the amplitudes of the vibrations vary over a great range, the average force acting on the electron space lattice cannot be obtained. As in the Wien theory it may be assumed that there is a law of repulsive force $kf(r)$ giving a resistance proportional to the square of the amplitude, and hence proportional to the energy E , since $E = \alpha A^2$

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where α is the quasi-elastic force holding the atoms in position. It can be shown¹ that α is roughly proportional to N , the number of electrons per unit volume, and hence the resistance is a function of N and k , which we may write $\phi(N, k)E$. Consideration of general dimensional analysis then indicates a formula of the type

$$\frac{1}{C} = W = \frac{\rho^{\frac{1}{3}}}{N^{\frac{1}{3}}k^{\frac{1}{3}}} E$$

where ρ is the density of the electron space lattice. As ρ , N , and k are independent of temperature (neglecting slight changes due to volume expansion), this requires W to be proportional to E in agreement with fact.

We have already indicated that the electron lattice theory regards the thermal conductivity as due to elastic waves passing down the lattice of electrons, as in the Debye theory of heat conduction. According to the Debye theory the limiting frequency of the electron lattice will be high, and is given by $\nu_m = \left(\frac{\nu}{4\pi}\right) \frac{1}{\rho^{\frac{1}{3}}\kappa^{\frac{1}{3}}}$ where κ is the compressibility. If the electron lattice is formed by the loss of one electron from each atom, we may put $N = \frac{n}{v}$ where n is the number of atoms, and hence the electron density Nm is given by

$$nm$$

where m is the mass of an electron.* The compressibility κ can be shown to be the same order as that of a solid, and is a function of N and the dielectric constant of the metal (D). According to a relation found by Haber the limiting frequency ν_m of the electron lattice is of the order $\sqrt{\frac{M}{m}} \nu'_m$ where M is the mass of the atom, and ν'_m the limiting frequency of the atomic lattice, and hence since $\frac{M}{m}$ is of the order 100 to 600, the limiting frequency of the electron lattice is very high, and an electron lattice at room temperature will correspond to an atomic lattice at only a few degrees above the absolute zero. Under these conditions the thermal conductivity will be very large, and the ordinary Debye

* These expressions are readily modified for cases in which more than one electron is liberated from each atom.

formula cannot be applied, since it refers to temperatures greater than the characteristic temperature $\theta_0 = \beta\nu_m$. According to this formula the thermal conductivity K , is given by

$$K = \frac{\rho q \gamma}{4} l$$

where ρ is the density, q is the velocity of sound, which equals $\frac{1}{\sqrt{\rho\kappa}}$, and γ is the specific heat, whilst l is a free path term representing the distance in which the energy of the elastic waves is diminished to the $\frac{1}{e}$ th part. But at temperatures which are only a small fraction of the characteristic temperature, the term l cannot be evaluated. Since, however, ρ , κ , and γ depend upon N and D , the term l will depend only upon (1) the number of layers of atoms per cm., i.e. upon $v^{\frac{1}{3}}$, (2) the temperature θ , and (3) the value of N . Hence we may write

$$K = \psi(N, D, \theta).$$

Experiments on the thermal conductivities of non-metallic substances at low temperatures, indicate that when θ is a small fraction of θ_0 , the conductivity does not vary with temperature, so that the above relation reduces to

$$K = \psi(N, D).$$

The constancy of the Wiedemann-Franz ratio therefore requires

$$K = \psi(N, D) \propto \phi(N, k) = \frac{C}{E}.$$

This is, of course, an *ad hoc* assumption made in order to agree with the Wiedemann-Franz Law, and the theory does not attempt to predict this. Considerations of dimensions indicate that the thermal conductivity K varies as $\frac{1}{N^{\frac{1}{3}}\rho^{\frac{1}{3}}\kappa^{\frac{1}{3}}}$.

The specific heat of the electron lattice is, however, negligible because its characteristic temperature is so high. The limiting frequency is given by

$$\nu_m = \left(\frac{9}{4\pi}\right)^{\frac{1}{3}} \frac{N^{\frac{1}{3}}}{\rho^{\frac{1}{3}}\kappa^{\frac{1}{3}}}$$

and in the case of silver this leads to a characteristic temperature $\theta_0 = \beta\nu_m = 94,000^\circ$, so that the specific heat at room tem-

perature is extremely small, and in this way the old difficulty in connexion with the specific heats is avoided.

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3. Emission Phenomena

The electron lattice theories have been applied to emission phenomena by Roy and by Weigle, and it has been possible to deduce the usual type of equations for the emission phenomena, by arguments based on the older quantum methods. According to the original method of Roy,¹ the individual electrons situated on the electron lattice can be treated in the same way as the ions or atoms in the Born-Karman theory of specific heats. In this case the energy content of the electron lattice may be written in the form

$$E = \sum_{i=1}^{i=3N} \frac{h\nu_i}{e^{\frac{h\nu_i}{k\theta}} - 1} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where the $3N$ quantities $\nu_1, \nu_2, \dots, \nu_{3N}$ are the frequencies of the N electrons forming the electron lattice, and since, as we have already indicated, the frequencies of an electron lattice will be large, the term $h\nu$ is large compared with $k\theta$, and the factor $\left(\frac{h\nu}{k\theta} - 1\right)$ may be put equal to $\frac{h\nu}{k\theta}$.

As we have shown in Chapter X, the ordinary principles of thermodynamics indicate that the equilibrium pressure of an electron gas outside the metal, varies with the temperature according to the relation

$$\log P = \frac{-L_0}{R\theta} + \int_0^\theta \frac{(C_{p \text{ gas}} - C_{p \text{ solid}}) d\theta}{\theta^2} + C \quad . \quad . \quad (2)$$

The assumption made by Roy is that owing to the high frequency of the electron lattice its specific heat will be zero, so that the equation may be written in the form

$$\log P = -\frac{L_0}{R\theta} + \frac{5}{2} \log \theta + C \quad . \quad . \quad . \quad (3)$$

Roy then assumes that the heat of evaporation can be identified with the photo-electric work function $h\nu_0$, and so applying

exactly the same arguments as we described in connexion with the electron gas theories, he obtains the relation

$$I = (1-R) \frac{2\pi m e k^2}{h^3} \theta^2 e^{-\frac{h\nu_0}{k\theta}} \quad . \quad . \quad . \quad (4)$$

where R represents the fraction of the electrons which are reflected.

In this paper the electron lattice theory was really only drawn on in order to justify the assumption that the specific heat of the electrons in the metal is zero, and it was assumed that only those electrons with frequencies greater than ν_0 could be emitted. Otherwise the theory was based on thermo-dynamics rather than on any detailed conceptions of an electron lattice.

In a later paper Roy² investigated the same problem from the point of view of the statistical mechanics developed by Fowler and Darwin,³ and showed that the same results could be obtained. In this paper the point of view adopted was that of a statistical equilibrium between an electron gas and the solid metal, and it was assumed that the external electrons formed an ideal monatomic gas, and were emitted from the solid with velocities distributed according to the Maxwell Law, whilst the electrons inside the metal were regarded as forming space lattices with heat energy distributed according to Planck's Law of Quanta. It was also assumed that the atomic lattices retained their individuality. On this basis the statistical methods gave expressions for the mean energies of the electrons at different temperatures, and the expression for the thermionic current was of the form

$$I = (1-R) \frac{2\pi m e k^2}{h^3 K_2(\theta)} \theta^2 e^{-\frac{\phi}{k\theta}} \quad . \quad . \quad . \quad (5)$$

where R is the fraction of the electrons reflected, and $K_2(\theta)$ is a function depending on the specific heat of the electrons in the electron lattice. By comparing the extent to which the atomic heats of the metals exceed the theoretical value $3R$, it was concluded that $K_2(\theta)$ was not very different from unity, so that expression (5) reduces to the same form as equation (4).

The electron lattice theory is thus able to account for the thermionic emission in quite as satisfactory a way as the older gas theories, and the difficulty in connexion with the specific heats is avoided.

Attempts have been made by Weigle⁴ to calculate the latent heat of evaporation of the electrons from the conception of an

electron lattice, and a good agreement has been claimed in the case of the alkali metals. In this work a metal is assumed to evaporate and condense in two ways, and the evaporation of the positive ions and negative electrons is separated for purposes of calculation, a positive ion being evaporated from the crystal for each negative electron taken out. In the first place the electrons are supposed to evaporate from the metal, absorbing the heat of evaporation (L), and leaving the positive ions on their original lattice. The positive ions are then supposed to evaporate absorbing a latent heat of evaporation of positive ions (M). The gaseous electrons and positive ions are then supposed to combine again to form the crystal with the evolution of the grating or lattice energy, V_R , so that $V_R = L + M$. In the second process the metal is supposed to evaporate as neutral atoms furnishing the known heat of evaporation D , and the neutral atoms are then ionized with the absorption of the energy (J) corresponding to the known ionization potential. The ions are then supposed to combine to form the crystal with the evolution of the grating energy V_R , so that $V_R = D + J$. Similar processes are then applied to a crystal of a salt of the metal with a halogen, in which the units are known to be the ions, and in which according to the theory of Born the crystal is held together by the attraction of the oppositely charged ions. Weigle again considers cycles in which one kind of ion is evaporated from the crystal leaving the other kind upon their lattice, and by introducing a term to allow for the change from the metal lattice to that of the salt, he obtains an expression for the latent heat of evaporation of the electrons from a metal in terms of the known ionization potential of the metal atoms, the latent heats of evaporation, and the grating energies of the salts which are known both from thermo-chemical data, and by calculation from Born's theory. The expression obtained involves the term which allows for the change from the metal lattice to that of the salt, and it is assumed that this can be neglected because the latent heats of evaporation of the positive ions of a given alkali metal from its different halides are nearly the same. This assumption may be criticized on the ground that in the salts we deal with structures in which the contact is between unlike ions (see p. 234), whilst in the metals the closing up process is stopped by the contact of like ions, so that the conditions are not really similar. It is also open to question whether it is justifiable to separate the evaporation process quite so sharply into that of positive and negative ions.

On the other hand in the case of calcium Weigle⁵ has calculated the work of emission from the point of view of the lattice theory combined with the Born theory of compressibility. It is assumed that the negative electrons occupy the same positions as the fluorine ions in calcium fluoride, and the energy is expressed by an equation of the usual type involving an attraction varying as an inverse square of the distance, and a repulsion as an inverse higher power. In this way by considering the potential energy of an electron within the metal, and by showing that in normal polycrystalline metal the work of emission is the mean of that for all possible crystal faces, Weigle calculates the work of emission as 2.17 volts, as compared with experimental values of from 2.2 to 2.4 volts, so that the agreement is quite satisfactory.

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4. Further Developments of the Lattice Theory

As we have already indicated (p. 230), the electron lattice theory has been modified by Thomson and Borelius, but as these developments have not led to any marked advance we shall only refer to them briefly.

In the line of approach adopted by Thomson,¹ the electrons were supposed to occupy a lattice interpenetrating that of the atoms, and by assuming rather arbitrary positions for the electrons, it was shown that the compressibilities could be calculated approximately. It was further suggested that electrical conduction involved not the movement of the whole electron lattice as was imagined in the original Lindemann theory, but the movement of long chains of electrons along the lines of the lattice. In this way although the individual electrons might vibrate with a high frequency, and so have a negligible specific heat, the chain as a whole might vibrate with a low frequency, and so account for the thermal conductivity, the average energy of each *chain* being $R\theta/2$. This gave a much smaller specific heat than the older theories in which the average energy of each individual electron was $\frac{3R\theta}{2}$, but the method led to little but speculation.

In the type of lattice theory developed by Borelius,² the electrons are supposed to occupy a lattice between the atoms, and the average energy of an electron is assumed to be proportional to the absolute temperature, but with a proportionality factor much less than that required by the equipartition theory. The energy of the electron may thus be written $u = c\theta$. To avoid the difficulties of a three-dimensional problem, Borelius considers a row of alternate atoms and electrons, the inter-atomic distance being $2r$. A row of this kind may give rise to a longitudinal stationary wave of wave-length $4r$, and as long as the vibration is strictly regular, it is assumed that no energy is given to the electrons, owing to the perfect symmetry of the forces. On the other hand if the vibration becomes irregular, energy interchange will occur. In spite of the fact that the electrons are situated on a lattice, each electron is regarded as associated with one atom, so as to give a doublet of moment er , and rotational energy $\frac{u}{3}$. This conception differs from that of the di-poles in the Thomson theory (p. 206), since the latter looked upon the di-poles as formed by the ions, whereas the doublets assumed by Borelius involve the ion and the valency electron. Under the influence of an external electric force, the doublets become polarized, and their moment is given by a relation due to Langevin³ according to which the moment J produced by a force X is given by

$$\frac{J}{J_m} = \frac{erX}{u}$$

where J_m is the value of J for complete polarization. The theory now assumes that under the action of the thermal vibrations, the electrons in spite of being on a kind of lattice, move a distance of $2r$ for each half vibration. Owing to the polarization there is a movement in the direction of the force, and the relation deduced for the specific conductivity is

$$C = \frac{1}{2}e^2 \frac{\nu}{ru},$$

Since the frequency ν is but little affected by the temperature, this implies that C varies as $\frac{1}{u}$ or as $\frac{1}{\theta}$. It can be shown that this kind of an argument gives much smaller values for the Thomson Heat than the older electron gas theories. The thermal conductivity is regarded as due to elastic waves in the atomic lattice

—not in the electronic lattice as in the Lindemann theory—and these waves are scattered or dissipated by interaction with the electrons. By using the Debye equation for thermal conductivity and assuming that the fraction of the energy given up at each interchange is equal to the ratio of the kinetic energy of an electron to that of an atom, the relation obtained for the thermal conductivity is

$$K = \frac{a^2 \theta \nu}{ru}$$

so that the Wiedemann-Franz ratio reduces to $\frac{K}{C} = 2 \left(\frac{a}{e}\right)^2 \theta$ as compared with the value $\frac{2}{3} \left(\frac{a}{e}\right)^2 \theta$ of the Drude theory. In a later paper the line of argument was slightly modified and the expression for the Wiedemann-Franz ratio became

$$\frac{K}{C} = 2 \frac{r}{R} \left(\frac{a}{e}\right)^2 \theta$$

where R is the distance between an electron and an atom, and $2r$ the distance between two neighbouring atoms.

As stated above, the theory imagines the electrons to move a distance of $2r$ for each half vibration of the atoms, and this motion is supposed to take place in a curved orbit, and by considering how the presence of a magnetic field might affect first the angular velocity, and secondly the radius of the curved orbit, it was possible to account for the existence of both paramagnetic and dia-magnetic metals, and also for positive and negative co-efficients for the Hall Effect, and in the left half of the Periodic Table the theoretical predictions were in general fulfilled, but the theory broke down in the case of the ferro-magnetic metals, and for the elements in the right half of the Periodic Table.

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5. Discussion

As will be seen from the preceding chapters, the electron lattice theory covers a wide range of facts in a general way, but as regards the electrical properties it has only been developed quantitatively in connexion with the emission phenomena. The

point of view adopted has in some cases been very plainly that in problems such as these of conductivity, the laws of force and other factors are so complex that little is to be gained by attempting to build a detailed quantitative theory until the facts are better known. In many ways this attitude is certainly justified, for there is little doubt that, in some of the other theories, vast and detailed mathematical superstructures have been erected upon assumptions which are obviously so very crude that the theories become of interest rather as abstract mathematical problems than from the point of view of physical science. But it is certainly unfortunate that more attempts have not been made to fill in, empirically or otherwise, some of the unknown constants in the very general equations which have been deduced for the lattice theory, for this lack of quantitative development has often resulted in the theory being dismissed as a mere hypothesis.

If once the conception of an electron lattice be accepted, the theory gives a satisfactory qualitative explanation of the electrical and thermal phenomena except those involving contact potentials and similar properties, where it seems rather more difficult to understand the flow of electrons from one metal to another if they form a static lattice than if they are moving more or less freely throughout the metal. But, on the whole, the lattice theory is in good agreement with the electrical and thermal facts, and satisfactorily overcomes the difficulties in connexion with the specific heats. The criticism of the theory on the grounds that while an electron lattice by itself may have the properties assumed, the same will not be true when it interpenetrates the atomic lattice, does not appear justified, since the widely differing frequencies of the electron and atomic lattices should prevent their interfering with one another appreciably.

From other points of view the theory is one of great interest in that it is almost the only one which has been extended to cover properties other than those of a purely electrical or thermal character. It seems to be well established that the conception of a metal crystal as built up of an electron lattice interpenetrating that of the atoms is able to give the right order of magnitude for the compressibility, and also, according to Weigle, for the work of emission. This does not, however, necessarily mean that the lattice is static, for as long as the attraction between an electron and an ion is proportional to $\frac{e^2}{r^2}$, approximately the same results

will be obtained by a dynamic lattice of the type suggested by Haber, in which there is a possibility of interchange of electrons from one point on the lattice to another.

The theory has been criticized by Bridgman on the grounds that in the case of the alkali metals, which crystallize with the body centred cubic structure, it is difficult to see how to fit one electron per atom into the unit cell in such a way that the symmetry remains cubic. This difficulty does not arise if there are three electrons per atom, but this is obviously impossible in the case of the alkalis. This criticism, however, does not appear justified, for, in the first place, by taking a larger unit cell it is quite possible to arrange an electron lattice interpenetrating a body centred cubic arrangement of atoms in such a way that cubical symmetry is retained, although the size of the unit cube is of course altered, whilst, apart from this, it is by no means clear that an atomic lattice of cubical symmetry must necessarily imply cubical symmetry for the atoms and electrons together. The *X*-ray methods of course reveal only the positions of the atoms, and do not show those of the electrons, so that on the whole it appears premature to criticize on these lines.

The modifications of the theory due to Thomson and Borelius have not led to any marked advance, although the method of Borelius is of interest as showing that the Wiedemann-Franz ratio can be predicted by means other than those involved in the conception of an electron gas. But, as pointed out by Bridgman at the Solvay Congress, there are difficulties in reconciling an electron lattice with the conception of electrons moving a distance $2r$ during each half vibration of the atoms, whilst the assumption that the mean energy of an electron is proportional to the absolute temperature, but with a proportionality factor much smaller than the equipartition value, is of course quite arbitrary.

The electron lattice theory is thus in an interesting and peculiar position. On the one hand it offers a general explanation of the electrical and thermal properties avoiding the difficulties of the older theories, and receiving satisfactory support from other spheres. But, on the other hand, the absence of quantitative developments in connexion with the electrical properties is inevitably a serious weakness. We shall discuss later (page 296) the question as to how far the lattice theory may really be an attempt to express the same ideas as those of the more recent theories due to Sommerfeld and Bloch which are described in the next chapter.

XIII

THE SOMMERFELD THEORY AND ITS LATER MODIFICATIONS

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1. General

THE Sommerfeld theory is the latest of the theories of the metallic state, and is in many ways the most difficult to describe in a general way, since it involves the new Quantum Mechanics. We shall therefore give a brief review of the theory, and also a general description of the new statistical methods before discussing the details.

In the preceding chapters we have seen how the attempts of Lorentz and others to elaborate the simple electron gas theory of Drude, led to a complete impasse from which there appeared to be no escape. On the one hand the optical properties indicated that the number of conducting electrons was of the same order as that of the atoms, and this appeared to be in direct contradiction to the results obtained from consideration of the specific heats. On the other hand if the evidence of the specific heats were accepted, and the number of conducting electrons assumed to be small compared with that of the atoms, the free paths required were so long that it appeared impossible to reconcile them with the general conceptions of a 'gas' theory. All these difficulties, however, really depend upon two underlying assumptions. The first of these, which we have already emphasized, is that the electrons obey the classical gas laws, so that their mean kinetic energy is directly proportional to the absolute temperature. The second assumption, which we have so far rather ignored, is that an electron when in motion can be considered as possessing only what we may call 'particle' properties. That is to say we have

looked upon an electron as a minute bullet, which differs only from a rifle bullet in respect of its size and its negative charge. The new Quantum Mechanics indicate, however, that the first of these assumptions is certainly incorrect, and that the second represents only one part of the truth. For, in the first place, the new statistics of Fermi and Dirac, which are a natural outcome of the Wave-Mechanics, indicate that if the electrons inside a metal do in any way represent a gas, the law of distribution, and the properties which depend upon it, will be quite different from those required by the older classical theory. Apart from this, however, the new theories indicate that electrons may be expected to possess properties not merely of 'particles', but also of waves, so that many properties which appeared impossible from a purely 'particle' point of view may be quite possible when the wave-like character of an electron is also taken into account.

The original papers of Sommerfeld¹ consisted in using the methods of the Lorentz theory, but in replacing the old classical mechanics and distribution law by the new wave-mechanics and Fermi-Dirac statistics. A brief indication of these methods will be given in the following section, but for the present we may note that the essential points are as follows. According to the classical distribution law, the mean energy of the electrons varies directly as the absolute temperature, whereas, according to the new equations, the electrons, at ordinary temperatures, are in such a condition that their energy is practically independent of temperature. In this way the specific heat difficulty is overcome, since rise of temperature produces a negligible increase in the energy of the electrons.

The actual velocity distribution according to the new statistics is also profoundly different from that required by the classical equations. According to the older Maxwell statistics, the majority of the electrons had velocities in the neighbourhood of the mean value, and the mean energy varied as the absolute temperature. But according to the new statistics, the velocities of the electrons in the 'electron gas' vary from zero to a certain limiting critical velocity, which is exceeded by only a few electrons, and, at ordinary temperatures, this critical velocity is almost independent of temperature. At the absolute zero of temperature the velocities of the electrons vary from zero to the critical value, which becomes a maximum value, but, as the temperature is raised, a small number of electrons have velocities above the critical value, and the velocity distribution of these

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few electrons is very nearly the same as that required by the Maxwell Law. The number of electrons with velocities above the critical value increases with the temperature, but at all ordinary temperatures the number is relatively small. The electrons are thus still regarded as moving about freely like the particles of a gas, although this gas is highly 'degraded' or 'degenerate'; that is to say it is in a condition in which the classical laws are no longer fulfilled. In particular the electron gas possesses energy at the absolute zero, since here the velocities are still distributed over a wide range, namely that from zero to the critical value referred to above.

If the theory is to be understood it is essential to appreciate the nature of this distribution law, which is described more fully in the following section.

When an electric force is applied, the electrons are supposed to acquire a general drift in one direction just as in the theories of Drude and Lorentz, and this drift is treated as a slight change in the distribution law, as in the Lorentz theory, except that the new equations are used in place of the old, with a correspondingly different mathematical treatment.

In this way the following expressions are obtained for the specific electrical conductivity, thermal conductivity, and the Wiedemann-Franz ratio:

$$\text{Specific Electrical Conductivity } C = \frac{8\pi}{3} \frac{e^2 \lambda}{h} \left(\frac{3n}{8\pi} \right)^{2/3} \quad (1)$$

$$\text{Specific Thermal Conductivity } K = \frac{8\pi^3}{15} \frac{\lambda k^2 \theta}{h} \left(\frac{3n}{8\pi} \right)^{2/3} \quad (2)$$

$$\text{Wiedemann-Franz Ratio} = \frac{\pi^2}{15} \left(\frac{K}{C} \right)^{-1}$$

From this it can be seen that the terms λ and n cancel out in the ratio of the conductivities so that equation (3) is obtained. The Lorentz expression (page 192) is of the same nature, but with a numerical factor $3/2$ instead of $\frac{\pi^2}{3}$. At 18°C . the Sommerfeld value for the Wiedemann-Franz ratio is 7.1×10^{10} , as compared with the Lorentz and Drude values of 4.2 and 6.3×10^{10} respectively. The Sommerfeld value is in slightly better agreement with the facts than that of Drude, but to some extent this is probably only a coincidence, since the values for the different metals vary by more than ten or even twenty per cent.

The next assumption made by the theory is that the number

of electrons taking part in the conductivity process is of the order one per atom. The grounds for this assumption are that, as described later (p. 297), it enabled Pauli to give the first satisfactory theoretical explanation of the magnetic susceptibility of the alkali metals, and also that it is in good agreement with modern views on valency and atomic structure. When the corresponding values of n are substituted in the above equations, it is found that the observed conductivities for the more common metals can only be accounted for if λ , the mean free path of an electron between two collisions, is of the order several hundred times the distance between two adjacent atoms. At first it may appear that this is a fatal objection to the theory, and many criticisms were in fact raised from this point of view, since it was argued that free paths of this magnitude were always considered impossible in the older theories. It is here that we have to remember the conceptions which are the result of the new mechanics. So long as we endow electrons only with the properties of 'particles', difficulties of this kind appear inevitable, but once we appreciate that electrons may also possess the characteristics of waves, we must recognize that quite a new set of properties may appear. We must no longer form a mental picture of a stream of electrons as consisting of a number of minute charged bullets in motion through the metal. Each electron is equivalent to a train of ψ waves,* and, whilst we may still consider the electrons as having a real existence, we must no longer imagine that this 'existence' implies only those properties which we associate with a 'particle' when we think of the latter in terms of the comparatively large objects with which our senses bring us into contact. Just as in optics, when we deal with light in bulk, we work in terms of rays of light travelling in straight lines, whilst, when we deal with things on a small scale, we have to

* The conception of the wave-like nature of an electron was introduced in the wave-mechanics of de Broglie and Schrödinger, and was at first a purely theoretical calculus or mathematical device which proved of great service in problems of atomic structure, particularly in connexion with the intensities of spectral lines. But more recently it has been shown by G. P. Thomson and by Davisson and Germer that when electrons strike metallic crystals, they do in fact give rise to diffraction patterns, which in the case of slow moving electrons agree with the wave length $\lambda = \frac{hm}{v}$ (m = the mass of the electron, and v its velocity) which is required by the wave theory. Space does not permit us to give any description of these theories here, and the reader who is interested should consult a book such as *Wave Mechanics*, by De Haas, or *Wave Mechanics*, by H. F. Biggs.

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use the wave theory, so with matter in motion, when we deal with large objects we can use the classical mechanics, and the mental pictures to which they give rise, but when we deal with individual electrons or atoms, we have to use the new wave-mechanics, and the results no longer agree with the mental pictures which we instinctively form when we think of 'particles' in motion.

Apart from this, there is an increasing tendency among physicists of the new school to argue that it is impossible for us to obtain a detailed mechanical picture of the individual process which any one electron undergoes. According to the Heisenberg Principle of Indeterminacy, even in an ideal experiment, we cannot determine accurately both the position and the velocity of an electron* simultaneously, and in the whole of the modern work on atomic structure as revealed by spectroscopy, the conclusion is that we must no longer attempt to 'explain' the individual processes by means of mechanical models. The whole tendency is to work in terms of probabilities, and to give up any attempt to follow events in detail. It may be objected that this point of view assumes too confidently that we are approaching finality in our experimental methods, for it must not be forgotten, that it was highly profitable to work in terms of the individual atom, long before there appeared to be any chance of detecting it experimentally. But whatever opinion we may form on this question, we cannot escape from the general conclusion that events on the atomic scale do not necessarily obey the laws which appear to govern actions between larger bodies. While, therefore, there may be many occasions on which it is still profitable to use some kind of a mechanical picture, we must realize that it may be quite unjustified to associate this picture with the principles with which we are familiar in reactions between comparatively large bodies.

At this stage the reader may meet with a difficulty. He may say that he is quite willing to accept the conclusion that electrons may possess wave-like properties, so that they can wind their way through the metal with free paths equal to several hundred times the inter-atomic distances, but he may quite reasonably ask how this conception can be reconciled with the assumption that the electrons can be treated as particles of an ideal gas, or with the very precise assumptions of collisions between spheres

* This follows from the fact that if we use radiation of very short wave length in order to measure the position accurately, the electron undergoes a 'Compton Effect', and its velocity is altered.

which the Lorentz treatment involves. The answer to this question is that the details of the calculations are but crude approximations from which we can only hope to obtain the correct order of magnitude. In all these problems we are in reality wanting to find two quantities. The first of these is the probability that the path of an electron will be appreciably interfered with, or in the words of the older theories, 'the chance of a collision', whilst the second quantity is the probable deflection which the collision will cause. In the Lorentz-Sommerfeld treatment, it is assumed that the electrons can be treated just as though they were particles of a gas contained in a box, and that they undergo collisions in which the probable deflection is that which would be given by collisions between spheres. At the same time the chance of a collision is taken into account by introducing the factors N , giving the number of atoms per unit volume, and R , representing the sum of the effective radii of the atom and electron during a collision, and the term λ^* is then used as an abbreviation for

$\frac{1}{\lambda^*}$, and can be identified as a free path, since the chance of a collision varies as πNR^2 . But this very precise treatment is of course only a crude approximation, and the very small value of R (or large value of λ) required in order to give the correct value for the conductivity is not to be taken as having a real physical meaning. The method is one in which the exact details of collisions between spheres are certainly wrong, but in which we may not unreasonably hope to obtain the right order of magnitude for the effect of the collisions. It became increasingly clear, however, that the treatment of the electrons as a simple gas was a very crude approximation, and that the complete theory must take into account the presence of the positive ions, and the fields of force to which they give rise.

The first attempt in this direction was due to Houston,² according to whom the scattering of electrons by collisions with the metal atoms can, from the point of view of the wave

* The free path term λ in the equation of Sommerfeld is not exactly the same as the free path of the older Lorentz theory. In the latter, the effective radii of the atom and electron during the collisions were assumed to be constant. But in the Sommerfeld theory the effective radius during the collision is a function of the velocity of the electron, and the mathematical analysis works out in such a way that the term $\lambda \left(= \frac{1}{\pi NR^2} \right)$ refers to a particular group of electrons, namely those with the highest velocities, and it is these electrons which essentially determine the conductivity.

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mechanics, be treated in the same way as the scattering of x-rays by a crystal lattice. Each electron corresponds to a train of ψ waves, and these may be considered as scattered by the crystal lattice in the same way as the scattering of x-rays. Since the wave lengths of the ψ waves corresponding to nearly all the electrons are larger than the lattice constants, it is considered that if, at low temperatures, the atoms were at rest, the wave trains corresponding to the electrons could pass down without interference, so that the free path would be very great. But when the atoms undergo thermal vibrations, the perfect symmetry is upset, so that interference occurs, and the resistance is created. In this way by assuming an arbitrary law for the field of force surrounding an ion, Houston obtains an expression for the effect of the scattering upon the velocity distribution, and shows that this can be made identical with the corresponding expression in the Sommerfeld treatment if the free path term λ in the latter is given by a certain equation. The value of λ obtained thus is then substituted in the Sommerfeld equation for the conductivity, and in this way a complicated expression is obtained for the specific conductivity, and the calculated values for a number of metals are found to lie within the limits ten times greater, or ten times less than the experimental figures. This method of approach is also in agreement with the fact that the resistance of non-cubic crystals varies with the orientation, since the scattering effect is only independent of direction in cubic crystals.

In the original paper of Houston it was assumed that the whole of the resistance was caused by the thermal vibrations of the ions, and consequently the resistance could only vanish at the absolute zero of temperature, if the thermal vibrations vanished also. There is, however, a great accumulation of evidence that the atomic vibrations still continue at the absolute zero, and that a zero-point energy ('Nullpunktenergie') persists, and it may at first appear that a resistance must remain at the absolute zero. Actually, however, the detailed investigation of the problem shows that this difficulty does not really arise. The conclusion reached is that the 'collisions' between the electrons and the atoms are not elastic, but that the electron always either loses or gains an amount of energy equal to $h\nu$, where ν is the frequency of the oscillator with which it collides. Consequently an electron can lose energy only when it can fall into a state of lower energy, and it can gain energy only when an oscillator can fall into a lower state, and as we shall see later, the restrictions imposed by

the new statistics indicate that at the absolute zero, the probability of scattering itself becomes zero, so that the resistance vanishes. In this respect the scattering of electrons is different from that of x-rays, since a beam of x-rays is not in thermal equilibrium, and so can give up energy to the atoms even at the absolute zero.

The method of Houston is, however, open to certain criticisms with which we shall deal later, and the problem has been investigated in great detail by Bloch.³ In this work it is assumed first, that the electrons move in a field of force which is strictly periodic, owing to the regular arrangement of the positive ions in the lattice, and the mutual interaction of the electrons is ignored (see p. 294). The motion of an electron under these conditions is then investigated from the point of view of the new mechanics, and the conclusion is reached that as long as the field is strictly periodic, the electron will be able to move unimpeded through the lattice so that the 'free paths' become infinitely long. But the thermal oscillations upset the strict periodicity, and in this way the resistance is created. The question is then treated as a disturbance problem of the interaction of the two coupled systems, the modified electron gas on the one hand, and the atomic lattice with its elastic vibrations on the other. The treatment is thus essentially the same as that of Sommerfeld, except that the electrons are assumed to move in a periodic field instead of forming a completely free gas, and the 'collisions' are considered in detail as interactions with the elastic vibrations of the crystal as a whole. The mathematical treatment naturally becomes involved, but as in the simple Sommerfeld theory it is assumed that the Fermi-Dirac equations give the normal distribution in the absence of an external field, and that in the presence of the field a new steady state is set up which differs but slightly from the normal. The final result is a complicated expression for the conductivity, and by assuming that the electrons have the velocities required by the simple Sommerfeld theory, it is shown that the right order of magnitude is obtained. This theory, and also that of Houston, requires the resistance, at high temperatures, to vary directly with the absolute temperature, and in spite of the zero-point motion of the atoms the resistance vanishes at the absolute zero for the same reasons as in the Houston theory.

The more complete theories of Bloch and Houston have not yet been applied to the problems of thermo-electricity and contact potentials, but the simple 'gas' theory of Sommerfeld has

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been extended in this direction, and although no satisfactory equation has been obtained for contact potentials, the new methods have led to expressions for the thermo-electric constants which are more satisfactory than those given by the older methods. For the Thomson Coefficient the expression obtained is

$$\mu = \frac{2\pi^2}{3} \frac{mk^2\theta}{eh^2} \left(\frac{8\pi}{3n}\right)^{2/3} \left\{1 - \frac{2}{3}\theta \frac{d \log n}{d\theta}\right\}$$

and this gives very much smaller values than the equations of the older theories, and is thus in much better agreement with the facts.

For the Peltier Coefficient the expression obtained is

$$\Pi = \frac{2\pi^2}{3} \frac{m(k\theta)^2}{eh^2} \left\{ \left(\frac{8\pi}{3n_2}\right)^{2/3} - \left(\frac{8\pi}{3n_1}\right)^{2/3} \right\}$$

where n_1 and n_2 are the numbers of electrons per unit volumes in the two metals which are in contact. This gives results of approximately the right order of magnitude, although the variation of Π with θ does not in general follow the simple square law which this equation requires.

By combining these two equations, the expression for the electromotive force of a thermo couple becomes

$$E_T = \frac{\pi^2}{3} \frac{mk^2}{eh^2} \left\{ \left(\frac{8\pi}{3n_1}\right)^{2/3} - \left(\frac{8\pi}{3n_2}\right)^{2/3} \right\} (\theta''^2 - \theta'^2)$$

according to which E_T varies as $(\theta''^2 - \theta'^2)$ whereas the older classical theory required a variation as $(\theta'' - \theta')$. The new equation again gives results of roughly the right order of magnitude, but the variation with temperature does not in general follow the $(\theta''^2 - \theta'^2)$ rule which the equation requires.

The general Sommerfeld theory has also been applied to the emission phenomena, and considerable success has been attained. In the first place, as pointed out by R. H. Fowler,⁴ the equations of the new statistics give a satisfactory explanation of the sharpness of photo-electric threshold frequency. We have seen that the Fermi-Dirac equations require the velocities of the electrons to be distributed from zero to a certain critical value which is exceeded by a comparatively few electrons. If ϵ be the energy of the electrons with this critical velocity, then $\epsilon = \frac{h^2}{2m} \left(\frac{3n}{8\pi}\right)^{2/3}$, and the energies of practically all the other electrons will be less than ϵ . Let us now suppose that light of frequency ν falls on the metal, and is absorbed by the electron which has to do an amount

of work χ_0 in order to escape. Then as long as $(h\nu + \epsilon)$, the energy of an electron after it has absorbed a quantum, is less than χ_0 , no electrons will be able to escape through the surface. But as soon as the frequency is sufficiently great to make $(h\nu + \epsilon)$ greater than χ_0 , the electrons with the critical energy ϵ will be able to escape. The sharpness of the threshold frequency is thus the result of there being practically no electrons with energies greater than ϵ , and the threshold frequency, ν_0 , will clearly be given by

$$h\nu_0 = \chi_0 - \epsilon.$$

The term χ_0 represents the work required to extract an electron from rest in the metal to rest at infinity, and is not the same as the usual thermionic work function, χ , which refers to equilibrium conditions, the relation between the two being

$$\chi = \chi_0 - \frac{\hbar^2}{2m} \left(\frac{3n}{8\pi} \right)^{2/3} = \chi_0 - \epsilon$$

so that $\chi = h\nu_0$ in agreement with fact.

The theory has also been applied to thermionic emission, the chief work in this connexion being due to Nordheim,⁵ and to R. H. Fowler.⁶ When the new statistics are used in connexion with the usual conception of an equilibrium between the electrons inside and outside a metal, the equation obtained for the emission current is of the form:

$$I = 120(1-r)\theta^2 e^{-(c-\mu)/k\theta}$$

where μ is a parameter equivalent to the partial potential of the electrons, and r represents the fraction of the electrons reflected at the surface. This equation is of the general form

$$I = C\theta^2 e^{-d/\theta}$$

and, as we have already seen (page 140), the numerical values for most pure metals indicate that C is of the order 60, suggesting that about one-half of the electrons striking the surface are reflected back. The factors affecting the reflexion process have been investigated in detail by Nordheim, and we shall refer briefly in section 7 to some of the results which have been obtained, since it is these which form some of the most striking successes of the new theories. The passage of an electron through the surface may be considered as involving a more or less abrupt change in potential, and Nordheim has investigated the passage of electrons through various types of boundary fields, when viewed in the light of the wave-mechanics. It is then found that

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when the wave-like properties of an electron are taken into account, it is possible for an electron to penetrate a surface, which, as regards its electric potential, would prevent the passage of an electron if the latter were considered as possessing only what we have called 'particle properties'. The first investigation of Nordheim indicated that the theoretical value of the reflexion coefficient was of the order $\frac{1}{2}$, in apparently excellent agreement with the above equation, but a more detailed examination showed that this was due to an undue simplification of the problem, and that the theoretical value of the term $(1 - r)$ was really very nearly unity, so that the theoretical value of the constant is more nearly 120 than 60, although the general order of magnitude is still obtained. On the other hand, the abnormal values of C given by some metals such as platinum (see p. 141) are at present unaccounted for. It has further been found possible to investigate the effect of thin films on the surface of the metal, and results of the greatest interest have been obtained, although we shall not refer to these here, since they concern what are really secondary phenomena, and not properties of pure metals.

The theory has also been applied to the case of the strong field emission, the chief work in this connexion being due to Houston,⁷ and to R. H. Fowler and Nordheim,⁸ who have shown that it is possible to deduce, for the emission current I , an equation of the type

$$I =$$

and this is indistinguishable from the empirical relation of Millikan and Gossling to which we have already referred in connexion with the experimental results (p. 145). The theoretical values, however, indicate that the emission should become noticeable for fields of the order 10^7 volts/cm., whereas actually the emission can be detected in considerably weaker fields. This discrepancy is, however, probably due to the fact, to which we have already referred (p. 144), that the emission does not proceed uniformly from the whole surface, but comes chiefly from small areas which, presumably, correspond to surface peaks or to impurities.

The Sommerfeld theory and its later modifications thus cover a very wide field, and in the following sections we shall consider some of the details.

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2. The New Statistical Methods

If the Sommerfeld theory is to be appreciated,* a general understanding of the new statistical methods and of the degradation theory of gases is essential. We shall therefore give a general description without going into the details, and for this purpose we shall adopt a rather simple and mechanical point of view.

The essential problem is the way in which the velocities of the different molecules of a gas are distributed, and in this connexion we again make use of the conception of a velocity diagram which, as we have already explained (p. 184), was first introduced by Maxwell. We may then consider any molecule with a particular velocity r , and if we refer the position of this molecule to rectangular co-ordinates x, y, z , we may resolve the velocity r into three components ξ, η, ζ parallel to the three axes, where

$$r^2 = \xi^2 + \eta^2 + \zeta^2.$$

We then imagine a second diagram to be drawn in which we take as co-ordinates the values of ξ, η , and ζ , so that the position of a point in this diagram gives, not the position in space of the particular molecule concerned, but its velocity components parallel to the three axes x, y, z . Working in this way the actual velocities of all the innumerable molecules of a gas will be represented in the velocity diagram by a vast number of points, and the distribution of these points in the velocity diagram gives the required velocity distribution of the molecules.

The older classical theory led to the well-known Maxwell Distribution Law, according to which the number of molecules per unit volume with velocity components between $(\xi\eta\zeta)$ and $(\xi+d\xi, \eta+d\eta, \zeta+d\zeta)$, or in other words the number of points in the velocity diagram lying in the element $(d\xi, d\eta, d\zeta)$, is given by

$$N \sqrt{\frac{q^3}{\pi^3}} e^{-q^2} d\xi d\eta d\zeta$$

where N is the total number of molecules per unit volume, and $r^2 = \xi^2 + \eta^2 + \zeta^2$, and q is a constant connected with the mean

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square velocity u_m , by the relation $q = \frac{8}{2u_m^2}$. This kind of distribution law requires the great majority of the molecules to have velocities in the neighbourhood of the mean value, and the mean energy varies directly as the absolute temperature. In this case, therefore, as the temperature is lowered, the mean velocity of the molecules becomes continually smaller, and vanishes at the absolute zero, where the theory requires the molecules to be at rest.

In the new statistical methods, the velocity diagram is divided into a number of little cells of which the centres give the values

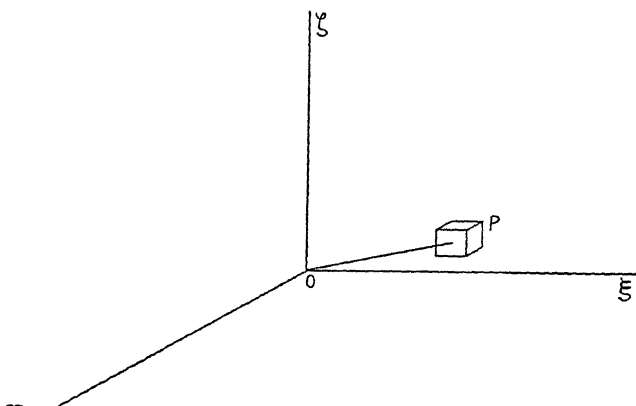


FIG. 49.

of the velocities corresponding to the different energy states. In a gas of volume V each energy state corresponds to a volume $\frac{h^3}{V}$, where h is Planck's constant, so that by taking a sufficiently large volume we can make the states as close together as we please, and for convenience we use components of momentum instead of the simple velocity components. That is to say, in Fig. 49, for example, each state corresponds to a unit cell such as that at P , and the number of molecules in this particular state will be given by the number of velocity points which are found in the cell at P . If the energy of a particular state is small, the corresponding cell in the velocity diagram will be near the origin, whilst if the energy is large, the cell will be far away.

The question then arises as to how many molecules occupy each state, or in other words how many points will be found in

each unit cell P in Fig. 49. In the classical statistics there were no restrictions in this connexion, and any number of points might be found in one cell. But in the recent statistics this is no longer the case, and the problem has been attacked in two main ways, the so-called Bose-Einstein, and Fermi-Dirac statistics. The Sommerfeld theory is concerned only with the latter and in order to understand this we shall consider briefly what is known as the *Pauli Exclusion Principle*.

It is well known that in the Bohr theory of atomic structure, the electrons occupy definite orbits which are characterized by distinct quantum numbers. According to Pauli, an electronic orbit is defined by four quantum numbers, n , l , m , and s . Of these n is the total quantum number, and is a measure of the energy of the orbit, l measures the orbital angular momentum, m the orientation of the orbit with respect to some plane, whilst s gives the angular momentum of the electron's spin, and is always equal to $\pm\frac{1}{2}$. The n term of Pauli is the same as the n term of the original Bohr theory, but the l in Pauli's notation corresponds to $(k-1)$ in the original Bohr notation, so that l may have any value from 0 to $(n-1)$. The third quantum number m may have any value from l to $-l$, including 0, so that for each value of l , there are $(2l+1)$ values of m . Pauli's exclusion principle then asserts that in any one atom, no two electrons can be in exactly the same state as defined by the same four quantum numbers. We may, for example, have one electron in that state characterized by the quantum numbers $(2, 1, 1, +\frac{1}{2})$ and one in that denoted $(2, 1, 1, -\frac{1}{2})$, but we cannot have 2 electrons in a $(2, 1, 1, +\frac{1}{2})$ orbit. By means of this principle it was possible to explain many points in connexion with atomic structure, and in particular to account for the presence of $(2, 8, 18, 32 \dots)$ electrons in the completed quantum groups. This can readily be seen, since if the principal quantum number, n , is, say 3, then when $l = 0$, and $m = 0$, $s = \pm\frac{1}{2}$ giving two electrons; when $l = 1$, the possible values of m are $-1, 0, +1$ for each of which $s = \pm\frac{1}{2}$, thus giving 6 electrons; whilst when l reaches its maximum value of 2, the possible values of m are $-2, -1, 0, +1, +2$ for each of which $s = \pm\frac{1}{2}$, thus giving 10 electrons. The total number of electrons when $n = 3$ is thus $2+6+10 = 18$, and similar considerations apply in the other cases.

Now in the problem of the distribution of velocities among the molecules of a gas, we have already seen that the quantum considerations require each molecule to be in a definite state, and

that each state corresponds to a cell of volume $\frac{h^3}{V}$ in our momentum diagram. It is now the at first sight rather striking conclusion of the Fermi-Dirac statistics that, just as in the single atom, according to the Pauli Principle, there is never more than one electron in a given state, so among all the molecules of a gas, there is never more than one molecule in a given state. Or in other words in our momentum diagram, each unit cell P can only contain one point. This conception was first put forward as a bold assumption, but was later shown to be a logical necessity of the quantum mechanics.

At high temperatures and low densities where the momentum points of nearly all the molecules are far from the origin in the momentum diagram Fig. 49, the above restriction makes comparatively little difference as compared with the older views, for there are innumerable cells which the momentum points may occupy. But at low temperatures the conception of the state of the molecules becomes quite different from that of the older theory. For since each state corresponds to a volume $\frac{h^3}{V}$ in the momentum diagram, and since only one molecule can be in a given state, it follows that even at the absolute zero of temperature only one molecule can be in the lowest state. The remaining molecules will have greater energies, and their momentum points in Fig. 49 will, at the absolute zero, occupy all the cells which are closest to the origin. There will therefore be a definite zero-point or 'Nullpunkt' energy, in contrast to the classical theory, in which the energy vanished at the absolute zero.

At slightly higher temperatures, nearly all the momentum points fill the cells nearest the origin in Fig. 49, and very occasional ones are in cells at a greater distance. In this way by assuming that there can never be more than one momentum point in any one cell in Fig. 49, but that each cell must either contain one point or no point, either event being equally probable, the Fermi-Dirac statistics lead to new and more complicated expressions for the distribution function and the energy.

There is, however, one further point which must be mentioned before proceeding to the actual equations. In the statistical methods referred to above, and in the original development of the Fermi-Dirac statistics, the molecules are treated as structureless, and are supposed only to contain translational energy. But in the case of an electron gas, the theories of the spinning electron

indicate that an electron has rotational as well as translational energy, so that in the presence of a field, although it sets itself with the axis of spin in the direction of the field, the rotation may be in either direction, and the angular momentum will be different in the two cases. In the above treatment, this may be allowed for by assuming that there are two momentum points in each unit cell in Fig. 49, instead of only one, and by introducing into the equations a factor G , which in the case of the electron gas is equal to 2.*

According to the distribution function of the Fermi-Dirac statistics the number (dn) of electrons in unit volume with velocities between the limits (ξ, η, ζ) , and $(\xi + d\xi, \eta + d\eta, \zeta + d\zeta)$ is

$$dn = G \left(\frac{m}{h} \right)^3 f \cdot d\xi \cdot d\eta \cdot d\zeta = 2 \left(\frac{m}{h} \right)^3 f \cdot d\xi \cdot d\eta \cdot d\zeta.$$

In this the distribution function f is given by

$$f = \frac{1}{\frac{1}{A} e^{\frac{\epsilon}{k\theta}} + 1},$$

where $\epsilon = \frac{mr^2}{2} = \frac{m}{2}(\xi^2 + \eta^2 + \zeta^2)$, and $A = e^{-z/k\theta}$ where z is the thermodynamic potential of 1 molecule of gas. The distribution function therefore depends upon the value of A , which in its turn depends upon the extent to which the gas is degenerate.

At high temperatures and low densities, when the gas obeys the classical laws, A is very small and is given by the relation

$$\frac{1}{A} = \frac{VG}{N} \frac{(2\pi mk\theta)^{3/2}}{h^3} = \frac{2V}{N} \frac{(2\pi mk\theta)^{3/2}}{h^3}$$

where N is the total number of molecules in volume V . In this case the distribution function f becomes simply

$$f = Ae^{-\frac{\epsilon}{k\theta}}$$

which is the Maxwell Distribution Law of the older theories. In this case ($A \ll 1$) the equation for the total energy of the electron gas according to the new statistics becomes

$$E = \frac{3}{2} N k \theta$$

which corresponds to the old classical value.

* This particular point was ignored by Sommerfeld in his first paper, with the result that the formulae for the conductivities differ by a factor of 2 in the two papers. This, of course, did not affect the Wiedemann-Franz ratio, a fact which indicates that the latter is not in all ways the best means of checking a theory.

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But at very low temperatures or high densities, A becomes very large, and to a first approximation is given by the relation

$$\log A = \frac{h^2}{2mk\theta} \left(\frac{3N}{4\pi V G} \right)^{2/3} = \frac{h^2}{2mk\theta} \left(\frac{3N}{8\pi V} \right)^{2/3}$$

or to a second approximation by the expression

$$\log A = \left(\frac{3N}{4\pi V G} \right)^{2/3} \left[1 - \frac{(2\pi mk\theta)^2}{12h^4} \right]$$

where $G = 2$ for the electron gas. In this case the expression for the total energy of the electron gas when $A \gg 1$ is

$$E = \frac{2\pi V G h^2}{3N} \left(\frac{3N}{4\pi V G} \right)^{5/3} \left[1 + \frac{5}{12} \frac{(2\pi mk\theta)^2}{h^2} \left(\frac{3N}{4\pi V G} \right)^{2/3} \right]$$

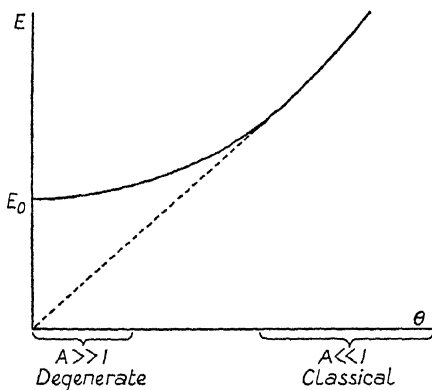


FIG. 50.

In this case, therefore, the energy does not vanish at the absolute zero, and, since $G = 2$, the zero point energy is given by

$$E_0 = \frac{4\pi V h^2}{5m} \left(\frac{3N}{8\pi V} \right)^{5/3}$$

The energy temperature curve corresponding to the above equation is of the form shown in Fig. 50, where the dotted line shows the variation according to the classical equations. At high temperatures and low densities, the new methods lead to the same results as the old, but at low temperatures this is not so, and when a gas has reached the point at which there is a perceptible difference between the curve in Fig. 50 and the dotted line representing the classical conception, the gas is said to be 'degenerate' or 'degraded', and when the curve becomes horizontal the

'degeneration' is complete; the corresponding German expression is 'Entartung'. With ordinary gases the temperatures at which these effects become noticeable are very low indeed. Thus with Helium, the effect may be expected to be appreciable at 5° Abs., but the calculations indicate that, if $n = \frac{N}{V}$ is the number of particles per unit volume, the conditions for degeneration may be expressed in the form
 Degeneration occurs if

$$\frac{nh^3}{2}(2\pi mk\theta)^{-3/2} \gg 1.$$

Whilst the classical conception is valid if

$$\frac{nh^3}{2}(2\pi mk\theta)^{-3/2} \ll 1.$$

From this it can be seen that the temperature at which degeneracy becomes marked will be very much higher as m , the mass of the particle, becomes less, and in this way it is calculated that an electron gas, if such exists, will at 36,000° C. be degraded to approximately the same extent as helium gas would be at 5° Abs. if it contained the same number of particles per unit volume. In other words if such a thing as an electron gas does exist, it will at ordinary temperatures be almost completely degraded, and the energy will be almost independent of temperature as in the horizontal part of the curve in Fig. 50.

In terms of our momentum diagram, Fig. 49, this means that in an electron gas nearly all the momentum points occupy the cells closest to the origin, and only very occasional ones are further away, and possess higher velocities. The electrons are thus still moving about freely like gas molecules, but their mean energy is almost independent of temperature. Further, since the momentum points are nearly all in the cells closest to the origin, there is a limiting velocity which is exceeded by only a very few particles, and as we have already noted it is this kind of distribution of velocities which, according to R. H. Fowler, provides the explanation of the comparatively sharp limiting frequency in the photo-electric effect.

Fig. 51 gives the kind of velocity distribution curve required by the new equations, the full line giving the distribution at the absolute zero of temperature, whilst the dotted line corresponds to a temperature of about 1,500° Abs. In this the function f (the probability that a cell in the region where the energy corresponds

to a velocity r shall contain a particle) is plotted against r , and it will be seen that the curve is characterized by a critical velocity in the neighbourhood of which the curve falls sharply, and this critical point plays an important part in the theory.

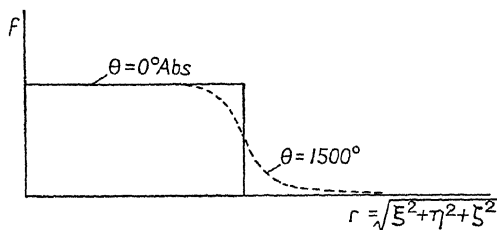


FIG. 51.

3. The Sommerfeld Equations for Electrical and Thermal Conductivity

In the general introduction to the theory we have already seen that the line of approach adopted by Sommerfeld is to use the method of Lorentz (chapter X) but to substitute the new distribution formula in place of the old. The results are then calculated on the assumption that the electron gas is completely degenerate ($A \gg 1$).

As in the older work we denote by $f_0(\xi, \eta, \zeta)$ the number of electrons per unit volume whose velocities, in the absence of an external field, lie within the limits (ξ, η, ζ) and $(\xi + d\xi, \eta + d\eta, \zeta + d\zeta)$. If then an electric force is applied in the direction of the x axis, we assume, as in the older methods, that this produces a slight disturbance of the distribution, so that the new distribution function $f(\xi, \eta, \zeta)$ may be written in the form

$$f = f_0 + \xi \chi \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The determination of χ is carried out just as in the Lorentz theory, so that if F is the external force the condition for the new stationary condition is given by

$$\frac{eF}{m} \frac{\partial f}{\partial \xi} + \xi \frac{\partial f}{\partial x} = b - a \quad . \quad . \quad . \quad . \quad (2)$$

where b and a represent the number of electrons which by collisions with atoms are either brought into or removed from the group whose velocities lie between the limits (ξ, η, ζ) and $(\xi + d\xi, \eta + d\eta, \zeta + d\zeta)$. In this way by using the Lorentz method, and assuming that the distribution in the absence of an electric field

is spherically symmetrical, the expressions deduced from the electrical and thermal conductivities are

<i>Sommerfeld.</i>	<i>Lorentz.</i>
$C = \frac{8\pi e^2 \lambda}{3h} \left(\frac{3n}{8\pi} \right)^{2/3}$	$\frac{4}{3} \frac{e^2 \lambda n}{\sqrt{2\pi m k \theta}}$
$K = \frac{8\pi^3}{9} \frac{\lambda k^2 \theta}{h} \left(\frac{3n}{8\pi} \right)^{2/3}$	$\frac{8}{3} \frac{\lambda n k^2 \theta}{\sqrt{2\pi m k \theta}}$

The Wiedemann-Franz ratio, according to Sommerfeld, is therefore

$$\frac{K}{C} = \frac{\pi^2}{3} \left(\frac{k}{e} \right)^2 \theta = 3.3 \left(\frac{k}{e} \right)^2 \theta.$$

In these equations, as in the Lorentz method, the term λ is an abbreviation for $\frac{1}{\pi n R^2}$, where n is the number of atoms per unit volume, and R the sum of the 'effective radii' of the electron and atom during a collision. Strictly speaking, therefore, λ is not a constant, but is a function of the electron velocity, because the evidence is that fast moving electrons can pass closer to the centre of the atoms than slow electrons. Sommerfeld* has, however, shown that, in the limiting case where $A \gg 1$, the mathematical analysis proceeds in such a way that the terms referring to the electrons with velocities on the horizontal part of the distribution curve in Fig. 51, do not remain in the final equation, and that the only term required is that giving the value of λ for those electrons lying at the critical point on the distribution curve, where the latter falls sharply. This is a peculiarity of the equations of the Fermi-Dirac statistics, and indicates that it is these electrons which essentially determine the conductivity. In the Sommerfeld theory, therefore, the free path term $\lambda \dagger$ is not exactly equivalent to the free path of the older theories, since the latter was considered as a mean constant value for the whole of the electrons, whereas the term λ in the equation of Sommerfeld refers only to those electrons lying at the critical point on the distribution curve, and to a first approximation the equations require the value of λ for these electrons to be independent of temperature.

It is here that the chief difficulties in connexion with the theory arise, since the expression for C does not contain the

* *Z. Physik*, 1928, 47, pp. 19, 23; *Naturwissenschaften*, 1928, 16, 378.

† In the original papers of Sommerfeld the term is called $l(v)$.

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temperature θ , whilst, according to the methods of calculation used, both n and λ are, to an approximation, constant. There is therefore nothing to account for the variation of C with θ , or for the fact that K is independent of temperature at ordinary temperatures. The correct value for the Wiedemann-Franz ratio is obtained, but the equations for the two conductivities are unsatisfactory, and, as pointed out by Sommerfeld, this implies that the conception of a 'free gas' is too simple, and that it is necessary to take into account the interchange of energy between the electrons and the atoms, and this is done in the later theories of Houston and Bloch.

The predicted value for the Wiedemann-Franz ratio is in very good agreement with the facts, and, if the observed values for the conductivities are substituted in the Sommerfeld equations, the value of λ is very large compared with the distance between two atoms. Thus for pure silver, $C = \frac{1}{1600}$ in c.g.s. units, and $n = 5.9 \times 10^{22}$ if each atom gives one free electron. Consequently $\lambda = 5.2 \times 10^{-6}$ cms., whilst the distance between two adjacent silver atoms is 2.88×10^{-8} cms., so that the free path is very large compared with the interatomic distances, and R the 'effective radius' during the collision is correspondingly small.

In the original theory of Sommerfeld, no explanation was given of the effect of temperature upon conductivity, but this was regarded as due to variations in λ and n which could not be calculated directly.

4. The Theory of Houston

We have already explained that the point of view adopted in this work is that the scattering of electrons by collision with the metal atoms can, on the basis of the wave mechanics, be treated in the same way as the scattering of x-rays, the difference being that the wave lengths of the ψ waves corresponding to nearly all the electrons are larger than the lattice constants, whereas the x-rays are of shorter wave length. It is therefore argued that if the atoms were at rest, and situated perfectly regularly in rows, the wave trains could pass down without interference, and that the free path would be infinitely great. The picture presented is thus very much like that of the older theories of Wien and Grüneisen.

In his first paper,¹ which gives results approximately valid for high temperatures, Houston adopts the same general point of

view as Lorentz and Sommerfeld, and writes the distribution function in the presence of an external force in the form

$$f = f_0 + \xi \chi(v) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\frac{eF}{m} \frac{\partial f}{\partial \xi} + \xi \frac{\partial f}{\partial x} - (b-a) = 0 \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where b and a represent the numbers of electrons which by collisions enter or leave the particular velocity group considered. It is then necessary to calculate b and a from the interference standpoint, and b is given by the relation

$$b = 8f(\xi\eta\zeta) \int (S \sin \vartheta d\vartheta d\varphi) \quad . \quad . \quad . \quad (3)$$

where S is the number of electrons which are scattered in the direction ϑ and φ , expressed as a ratio of the total number of incident electrons.

Similarly
$$a = 8 \int f(\xi'\eta'\zeta') S \sin \vartheta d\vartheta d\varphi \quad . \quad . \quad . \quad (4)$$

We consider only elastic collisions, and in (3) the integration over the unit cube gives all electrons which suffer a change in direction without a change in energy, whilst in (4) the integral gives all the electrons with velocity components (ξ', η', ζ') which by collisions are scattered into the first group.

In order to obtain S , use is made of an expression deduced by Debye and Waller for the interference of x-rays, and in this way the expression corresponding to (2) becomes

$$\frac{eF}{m} \frac{\partial f}{\partial \xi} + \xi \frac{\partial f}{\partial x} = -16\chi(v)\Re P \int S_1(\cos \vartheta - 1)(\xi' - \xi) \sin \vartheta d\vartheta d\varphi \quad (5)$$

where \Re is the total number of atoms in the metal, S the scattering caused by one ion, and P is given by

$$P = \frac{3}{l^2} \frac{h^2}{k} \frac{L}{A\theta_0} \cdot \frac{1}{x^2} \int_0^x \frac{\xi d\xi}{e^\xi - 1} \quad . \quad . \quad . \quad . \quad (6)$$

where L is the Loschmidt number, A the atomic weight, θ_0 the characteristic temperature of the metal, and $x = \frac{\theta_0}{\theta}$, and $l = \frac{h}{mv}$.

The above equation (5) will only enable us to obtain the $\chi(v)$ which is required in equation (1), if the integral can be evaluated, and this requires special assumptions as to the fields of force round the ion. Before dealing with these assumptions we may note that the general method gives some indication of the variation of the resistance with temperature. Since f and f_0 are the distribution functions in the presence and absence of an electric

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field, and since these are connected by equation (1) the total flow is given by

$$I = e \iiint \xi f(\xi, \eta, \zeta) d\xi d\eta d\zeta = \frac{4\pi}{3} e \int_0^\infty v^4 \chi(v) dv.$$

It can be shown that in this integration the temperature θ occurs only in the form of the function P (equation (6)) in the denominator, so that I , the current, is inversely proportional to P , and the specific resistance is directly proportional to P , so that

$$\text{if we write } \Phi(x) = \frac{1}{x^2} \int_0^x \frac{\xi d\xi}{e^\xi - 1}$$

$$W \propto P \propto \frac{1}{\theta_0} \Phi(x).$$

Hence when $\theta \gg \theta_0$ (or $x \ll 1$) we have from (6)

$$\Phi(x) = \frac{\theta}{\theta_0}.$$

So that $W \propto \theta$ in agreement with fact.

In order to obtain the value of $\chi(v)$ from equation (5), it is necessary to make special assumptions for the field of force surrounding the ions. The simple assumption of a Coulomb field cannot be used, and it is assumed, largely empirically, that the law which holds is of the form

$$U = \frac{Ze}{r} e^{-r/b}$$

where Ze is the charge of the ions, r is the distance, and b is a constant which, from considerations of the crystal structure of solid hydrogen, is empirically assumed to be one-sixth of the distance between the atoms (or ions) in the metal crystal.

From these assumptions by means of an analysis which we shall not follow here, an expression is deduced for $\chi(v)$, and this can be made identical with the expression for $\chi(v)$ in the Sommerfeld-Lorentz theory if the 'free path' in the latter is defined by the relation

$$\lambda = \frac{kA^2\theta_0 v^2}{24\pi Z^2 e^2 d L^2 H(c) \Phi(x)}$$

and when this is substituted in the Sommerfeld equation for the specific conductivity, the final result is

$$C = 4.42 \times 10^{12} \frac{\theta_0 d^{1/3} A^{2/3}}{Z^{2/3} \Phi(x) H(c)} \text{ (in electrostatic units).}$$

Here

θ_0 = the critical temperature. A = the atomic weight.

d = the density. Z = the charge on the ions.

$\Phi(x)$ = the function previously described, $\frac{1}{x^2} \int_0^x \frac{\xi d\xi}{e^\xi}$

$$= \frac{\theta}{\theta_0}.$$

$H(c) = (1+2c)/(1+c) - 2c \log (1+c)/c.$

$c = l^2/(4\pi b)^2.$

l = electronic wave length.

b = the previous constant determining the range of the ionic field.

It will be noted that in the Houston equation the term representing the number of electrons per unit volume does not appear directly. The reason for this is that Houston assumes the number of electrons to be some simple multiple of that of the atoms, so that if n be the number of electrons per unit volume, we may write

$$n = \frac{ZLd}{A}$$

where Z is the degree of ionization, and L the Loschmidt number.

The above very complex expression for the electrical conductivity can be compared directly with the experimental values if the number of free electrons per atom be assumed, and in this way Houston showed that by assuming reasonable degrees of ionization, the calculated values for a number of metals were within the limits ten times greater or ten times smaller than the actual values. But critical comparison can hardly be made, and it is by no means clear as to how much of the approximate agreement is not due to the choice of the particular law of force, and of its constants, which are assumed in the calculations.

The above work is thus an extension of the simple treatment of Sommerfeld, so that an expression is obtained for the mean free path λ , and it is assumed that the values obtained in this way by the wave scattering and quantum methods may be united with the Sommerfeld equations, although these are deduced by the Lorentz method in which the outlook is rather different.

At low temperatures, however, the above method is no longer justified, for the exact comparison between the scattering of

NOTE.—To facilitate comparison with the original, the electron velocity is denoted v throughout this section.

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electrons and of x-rays cannot be maintained. According to Brillouin² the light reflected from an elastic wave has a frequency equal to the sum or the difference of the frequencies of the incident light and the elastic wave. If the same applies to the scattering of electrons, then, since the frequency of an electron wave is proportional to its energy, the 'collisions' of the electrons are not elastic, but always result in the electron gaining or losing an amount of energy equal to $h\nu$, where ν is the frequency of the elastic wave with which the collision takes place. As we shall see in the next section, this conclusion was first reached independently by Bloch. It is here that the difference between the scattering of x-rays and of electrons becomes apparent. For the x-rays are not in thermal equilibrium, and so can always lose energy, but the electrons are in thermal equilibrium, and subject to the restrictions of the Fermi-Dirac statistics. An electron can therefore only undergo a collision in which it takes up energy if (a) there is a vacant state of higher energy to which it can jump, and (b) the oscillator is not in its lowest energy state so that it can give up energy. On the other hand in collisions in which the electron loses energy, the condition of the oscillator is unimportant, but there must be a vacant state of lower energy into which the electron can fall.

From the Sommerfeld theory, Houston³ assumes that the free path λ , which is in general a function of the velocity of the electron, can be replaced by the value $\lambda(\bar{v})$, where (\bar{v}) is the critical velocity at which the distribution curve falls sharply. Houston assumes further that only electrons with velocities in the neighbourhood of (\bar{v}) need be considered, and that after an impact these will have the energy $(\frac{1}{2}mv^2) \pm h\nu$. The restrictions to which we have referred above, then indicate that the probability that these electrons will be scattered at low temperatures is proportional to $1/(e^{h\nu/k\theta} + 1)$, so that at the absolute zero, where $\theta = 0$, the probability is zero, and no scattering can take place.

In order to apply this restriction to the determination of the resistance, we have to take into account the zero-point energy of the lattice, and by using an equation deduced for the scattering effect by Frenkel and Mirolubow,⁴ Houston shows that the free path λ is given by the relation

$$\frac{1}{\lambda} = \frac{2\pi Z^2 e^4 n^2 \kappa \theta_0 k}{m^2 v^4} \frac{1}{x_0} \int_0^{x_0} \frac{x^4 dx}{(e^x - 1)(x^2 + ax_0^2)^2}.$$

In this expression Z is the charge on the ion, n the number of

atoms per unit volume, k the compressibility, and θ_0 the characteristic temperature. If q is the reciprocal of the wave-length of the incident electron wave, Q the reciprocal of the wave-length of the elastic wave which causes the scattering, and if $c = 1/16\pi^2 q^2 b^2$ where b is a measure of the extent of the ion, $4q^2 c = aQ_1^2$, and the terms x and x_0 are given by $x = h\omega Q/k\theta$, and $x_0 = h\omega Q_1/k$ where ω is the velocity of the elastic wave in the crystal.

The exact limits of integration are rather uncertain because the vibrations are not sinusoidal, but the equation shows that the resistance vanishes at the absolute zero. At other temperatures the rate of change of resistance depends upon the factor a . If a is large, that is if the scattering is the same in all directions, the equation requires the resistance to increase as the fifth power of the temperature at low temperatures, and directly as the temperature at higher temperatures. But when a is very small the resistance is proportional to the absolute temperature at low temperatures.

The equation can be expanded for values of x_0 which are not too large, and in this way by assuming a to be equal to 0.1, Houston obtained the values of λ for gold, and showed that, when these were substituted in the Sommerfeld equation, the correct order of magnitude was obtained for the conductivity. These methods are not, however, so complete or satisfactory as those of Bloch, and reference to the original paper must therefore be made for the details.

The Effect of Pressure upon Conductivity.

In the original papers of Sommerfeld the effect of pressure upon conductivity was regarded as due to changes in λ and n , and it was considered that the changes were due not so much to variations in λ , the mean free path, as to an increase in n the number of free electrons. In the work of Houston, on the other hand, the possible changes in the number of free electrons are not considered, apart from the effect due to the change in volume, since all the ions are assumed to have the same charge. The pressure effect is thus regarded as due chiefly to changes in λ , and from this point of view the problem was first attacked approximately by Houston, and later more thoroughly by Waterman.⁵

If we denote the specific resistance by W , the Houston expression for conductivity may be written in the form

$$W = \text{constant} \times \frac{\Phi(x)H(c)}{\theta_0 d^{1/3}} \cdot \cdot \cdot \cdot \cdot \quad (1)$$

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if we assume that the charge on the ions is not affected by pressure.

So that the terms which may vary under pressure are $\Phi(x)$, $H(c)$, θ_0 , and d . Actual measurements involve the change in resistance of the specimen R , instead of the change in specific resistance W , and since $d(\log d) = -d(\log V)$ we may for convenience write

$$(\partial \log R / \partial p)_\theta = (\partial \log W / \partial p)_\theta - \frac{1}{3}(\partial \log V / \partial p)_\theta \quad (2)$$

In the method developed by Waterman the general arguments used by Grüneisen (see p. 214) are adopted, and it is assumed that the temperature is sufficiently high for $\Phi(x)$ to be replaced by θ/θ_0 . In this case, since the derivative at constant entropy (s) of any function of θ/θ_0 vanishes, we may put

$$(\partial \Phi(x) / \partial p)_s = 0$$

and we then have from (1)

$$\left(\frac{\partial \log W}{\partial p} \right)_s = \left(\frac{\partial \log H(c)}{\partial p} \right)_s - \left(\frac{\partial \log \theta_0}{\partial p} \right)_s - \frac{1}{3} \left(\frac{\partial \log V}{\partial p} \right)_s. \quad (3)$$

Using relations (3) and (2), and transferring from adiabatic to isothermal compression, remembering that $\left(\frac{\partial \theta}{\partial p} \right)_s = \theta / C_p \left(\frac{\partial V}{\partial \theta} \right)_p$, the final expression obtained is

$$\frac{1}{R} \left(\frac{\partial R}{\partial p} \right)_\theta = \left(\frac{\partial \log H(c)}{\partial p} \right)_\theta - \frac{\beta}{c'd} \left[1 + \theta \left(\alpha - \frac{\partial \log H(c)}{\partial \theta} \right) \right]. \quad (4)$$

where $\alpha = \left(\frac{\partial \log R}{\partial \theta} \right)_p$, and $\beta = \left(\frac{\partial \log V}{\partial \theta} \right)_p$, and c' = the specific heat per gram.

This expression is the general equation for the effect of pressure upon resistance, and it involves the variation of the function $H(c)$ with pressure, and this in its turn involves the effect of pressure upon the constant b in the equation $U = \frac{Ze}{r} e^{-r/b}$ assumed by Houston for the field of force surrounding an ion. Waterman has investigated two cases, in the first of which b is assumed to remain constant under pressure, whilst in the second case b is assumed to vary directly as the mean distance between the atoms. The better agreement is obtained if b is treated as a constant, and in this way the right order of magnitude is obtained for the pressure coefficient of the normal metals, but the positive pressure coefficients of the abnormal metals can only be

accounted for if the ratios between b and the interatomic distance are quite different from those in ordinary metals.

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5. The Theory of Bloch

In the preceding section we have seen how the work of Houston was a preliminary attempt to give a precise meaning to the free path term λ , which was introduced in the Sommerfeld 'electron gas' theory. In the method developed by Bloch,¹ the problem is attacked from a somewhat different angle, and a more satisfactory solution is obtained, although numerous approximations have to be introduced. The point of view adopted here is that whilst the conducting electrons are free, their motion is not completely haphazard as imagined in the 'gas' theories, but is rather a motion in a periodic field of force, of which the period is the same as that of the atomic lattice. The new mechanics then indicate that, as long as the field of force is strictly periodic, the electrons are able to move unimpeded through the lattice of the atoms (or more properly ions), and that it is only when this strict periodicity is upset by the thermal oscillations that a resistance is created. We have thus, first, to consider the motion of an electron in a periodic field, and, secondly, how the electrons may interact with the atomic lattice. The great step forward which is made in this theory is that the problem is treated, not as the scattering of electrons by single atoms, but as the interaction with the atomic lattice and its characteristic vibrations as a whole, and since an electron must always be in the field of several atoms at once, this method is clearly more satisfactory. The theory ignores all mutual interaction between the electrons, and the limitations which this involves are discussed later (p. 294), but even in this form the mathematical details tend greatly to obscure the argument, and for this reason we shall only give here a very general outline, the details being reserved for the Appendix (p. 343).

Using the methods of the new mechanics the amplitude of probability $\psi(xyz)$ which corresponds to the energy E , and is independent of time conforms to the differential equation

$$\Delta\psi + \mu(E - V)\psi = 0 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

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where V is the electrostatic potential in which the electron moves in the lattice, and $\mu = \frac{8\pi^2 m}{h^2}$. The first step is thus to obtain

the proper solutions of this equation for the electrons in the periodic field of the lattice, and these depend upon the boundary conditions to which they must conform. For this purpose we assume for the amplitude of probability of the electrons in the lattice, a cyclic condition similar to that used by Born and Karman for the elastic frequencies in their work on the specific heat of a crystal lattice. From this point of view the properties are known for the whole lattice provided they are known for a sufficiently large parallelepiped which may be defined by the vectors $G_1\mathbf{a}$, $G_2\mathbf{b}$, $G_3\mathbf{c}$, where G_1 , G_2 , G_3 are large integers. If therefore we know a property for the fundamental parallelepiped $G_1\mathbf{a}$, $G_2\mathbf{b}$, $G_3\mathbf{c}$, we can obtain it for the whole lattice by simple periodic repetition. The particular value of this method of treating ψ waves similarly to elastic waves is found when we deal with the interaction of the two kinds of waves which causes the electrical resistance.

The analysis then indicates that the proper function for the motion in a periodic field is of the form

$$\psi_{klm} = e^{2\pi i \left(\frac{kx}{K} + \frac{ly}{L} + \frac{mz}{M} \right)} u_{klm}(xyz) \quad . \quad . \quad . \quad (2)$$

where the function $u_{klm}(xyz)$ depends only on the periodicity of the lattice. In this expression k , l , and m are whole numbers corresponding to the state of the electron, and K , L , and M are the lengths of the vectors which define the fundamental parallelepiped. The expression for the proper functions can thus be split up into the factor $e^{2\pi i \left(\frac{kx}{K} + \frac{ly}{L} + \frac{mz}{M} \right)}$, and a remainder depending only on the periodicity of the lattice, and this means that we are concerned with plane de Broglie waves which are modulated in the rhythm of the lattice. It is this similarity of the proper function to that of the motion of an electron in the absence of forces which gives the electrons the mobility necessary for conductivity.

The Schrödinger theory then indicates that in general the state (k, l, m) corresponds to a definite momentum or velocity in the x direction,* and this can be investigated for the case of completely free, or very strongly bound electrons. In the former case

* The positions of the electrons are referred to the co-ordinates (x, y, z) , and the origin is assumed to be at a lattice point, so that if \mathbf{a} , \mathbf{b} , \mathbf{c} , are the fundamental lattice vectors, the vector of any lattice point is given by $\mathbf{G} = g_1\mathbf{a} + g_2\mathbf{b} + g_3\mathbf{c}$ where g_1, g_2, g_3 are whole numbers.

the current in the x direction corresponding to the state (k, l, m) is given by

$$e k h \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $\frac{kh}{K}$ gives the momentum corresponding to the wave length $\frac{K}{k}$. In this extreme case the modified plane de Broglie waves actually become plane waves.

The case of tightly bound electrons is very much more complex, and is treated by considering equation (1) as a disturbance problem of the same nature as that discussed by Heitler and London for the case of two hydrogen atoms, but whereas the work on the hydrogen molecule was a two-body problem, the theory of Bloch, since it ignores the mutual interaction of the electrons, is developed as a one-body problem. The analysis then indicates that for the strongly bound electrons, the expression corresponding to (3) is

$$S_{kim}^x = e \frac{ah\Phi^x}{\pi m} \sin \frac{2\pi k}{G_1} \quad . \quad . \quad . \quad . \quad (4) \quad (\text{Appendix, equation (20)})$$

where Φ^x is a complicated function (see Appendix, equation (18)).

We have next to consider the way in which the electrons will accelerate under the influence of an external electric force, and for this purpose we assume a wave packet similar to those considered by Heisenberg and Kennard, and investigate its motion in the x direction (i.e. under an additional potential $-eFx$) by a method introduced by Dirac. The analysis then indicates that the alteration in the distribution function f may be written in the form

$$\frac{df(\xi\eta\zeta)}{dt} = -\frac{2\pi eF}{h} \frac{\partial f(\xi, \eta, \zeta)}{\partial \xi} \quad . \quad . \quad . \quad . \quad (5)$$

(Appendix, equation (36))

This equation corresponds to that used by Lorentz and Sommerfeld, except that the terms ξ, η, ζ are no longer the simple velocity components, but are more complicated quantities connected with the velocities, and also characterizing the quantum states.

Up to the present we have only considered the motion of the electrons in a strictly periodic field, and under these conditions the electrons can move unimpeded through the lattice. From this point of view the appearance of an electrical resistance is due to an interaction between the electrons and the thermal vibrations of the atoms, and this may be treated as a disturbance problem

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of the interaction of the two coupled systems, the electron gas on the one hand, and the atomic lattice with its elastic vibrations on the other. The problem is highly complex, and for simplification it is assumed that the temperature is low enough for the elastic waves to be long compared with the interatomic distances, so that the crystal can be considered as continuous in respect to them, whilst the amplitudes are assumed to be so small that the vibrations can be considered as harmonic. The analysis then indicates that if at a time $t = 0$, an electron is in a state $(k'l'm')$, and the lattice in a state characterized by $q'(fghj)$ $r'(fghj)$, the probability that, at the time t , scattering or interaction has taken place in such a way that the whole system is in the state (klm) $q(fghj)$ $r'(fghj)$, is given by an equation (Appendix, equation (44)) which assumes a large value only if the expressions $E_{klm} - E_{k'l'm'} \pm \hbar\nu(f_1g_1h_1j_1)$ are small, where E represents the energy of the electron, and ν the frequency of the atom. In other words the essential scattering processes are those for which, to an approximation,

$$E_{klm} - E_{k'l'm'} = \pm \hbar\nu(f_1g_1h_1j_1)$$

and, as in the later developments of the Houston theory, the conclusion is that the 'collisions' which produce the resistance are not elastic, but involve an interchange of energy, equal to $\hbar\nu$, between the lattice and the electron.

As in the Lorentz and Sommerfeld method we may write the conditions for the steady state in the presence of an external field in the form

$$f(\xi\eta\zeta) = f_0(\xi, \eta, \zeta) + \xi\chi(\rho)$$

where χ is a small function of $\rho = \sqrt{\xi^2 + \eta^2 + \zeta^2}$ alone, and we have to determine χ so that a stationary state is set up under the joint influence of the external force, and the interaction with the atomic lattice, and then, when χ has been determined, the method of Lorentz and Sommerfeld may be used in order to obtain the expression for the conductivity. In this way the analysis leads to the following equation for the specific conductivity σ

$$\sigma = \frac{4(6\pi^2\kappa)^2}{3\pi^5} \cdot \frac{e^2 d \tau \omega v a^2 \mu^2}{m C^2 \hbar} \left(\frac{\hbar v}{ak\theta_0} \right)^5 \frac{\theta_0}{\theta} \quad (\text{Appendix, equation (65)})$$

In this d is the density and $\rho_0 = \sqrt{6\pi^2\kappa}$ is the critical velocity on the distribution curve, and again it is the electrons with this velocity which essentially determine the conductivity. The momentum in the x direction is given by $\tau \frac{2\pi\hbar}{G}$, so that $\frac{\tau}{m}$ is of

the order of the maximum velocity of the electrons, and in the free electron gas of the Sommerfeld theory this velocity is of the order 10^8 cm./sec. We may write this in the form $\frac{\tau}{m} = \tau' \cdot 10^8$, and assume that, in the case of the partly bound electrons which actually exist in metals, $\tau' = \frac{1}{10}$. The energy corresponding to the state klm is given by

$$E_{klm} = \omega \left[\left(\frac{2\pi k}{G} \right)^2 + \left(\frac{2\pi l}{G} \right)^2 + \left(\frac{2\pi m}{G} \right)^2 \right]$$

and ω is an energy of the order $\beta' 10^{-12}$ erg. where β' represents the effect of the interchange, and may be assumed to be about $\frac{1}{10}$. v is the velocity of propagation of waves, $\mu = \frac{8\pi^2 m}{h^2}$, C is the square of the reciprocal of a length of the order of the atomic radius (i.e. 10^{-8} cm.), and $\left(\frac{h\nu}{ak\theta_0} \right)$ is a number of the order unity. If we assume the temperature θ to be three times the characteristic temperature θ_0 , this requires σ to be of the order 10^{18} e.s.u. which is roughly of the right order of magnitude.

At moderate temperatures, the conductivity is proportional to $\frac{\theta_0}{\theta}$ where θ_0 is the characteristic temperature.

At very low temperatures, however, the conclusions are different for the reasons which we have already discussed in connexion with the Houston theory. Since the collisions involve an interchange of energy equal to $h\nu$ between the electron and the lattice, the restrictions of the Fermi statistics diminish the probability of scattering at very low temperatures, and at the absolute zero, the probability of scattering vanishes. The calculations require the resistance at very low temperatures to increase as the fifth power of the absolute temperature, and this is approximately true, although not in such good agreement with the facts as the Grüneisen law which requires a variation as the fourth power of the absolute temperature.

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6. Thermo-Electric Effects

The more complete theories of Houston and Bloch have not yet been applied to the problems of thermo-electricity and contact potentials, but expressions have been deduced by means

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of the Sommerfeld electron gas theory. In the original paper of Sommerfeld an expression was obtained which gave the right order of magnitude for the contact potentials, but the sign of the potential was wrong, and although these difficulties have been discussed by Eckart,¹ no satisfactory solution has been given.

As regards the thermo-electric effects, the Lorentz-Sommerfeld method² leads to the following two expressions for the flow of electricity and of heat,

$$J = \frac{16\pi em}{3h^3} k\theta V_0 \left\{ eF - 2k \frac{\partial \theta}{\partial x} \frac{V_1}{V_0} - k\theta \frac{\partial \log A}{\partial x} \right\} \quad (1)$$

$$W = \frac{32\pi m}{3h^3} (k\theta)^2 V_1 \left\{ eF - 3k \frac{\partial \theta}{\partial x} \frac{V_2}{V_1} - k\theta \frac{\partial \log A}{\partial x} \right\} \quad (2)$$

where V_0 , V_1 , and V_2 are functions which depend on the way in which the free paths of the electrons vary with the velocity. The nature of this variation is at present undetermined, and in the simpler developments of the theory the free paths are assumed to be independent of the velocity.

We now consider a flow of heat and electricity down a wire whose length is taken as parallel to the x -axis. The electrical work done in unit time is then JF , where F is the potential gradient, and of this the amount carried away by the energy stream is equal to $\partial W/\partial x$, so that the energy remaining is given by

$$Q = JF - \frac{\partial W}{\partial x} \quad (3)$$

Using the equations (1) and (2), and the previous expression for the electrical and thermal conductivities, we obtain the equations

$$W = \frac{2k\theta}{e} \frac{V_1}{V_0} J - K \frac{\partial \theta}{\partial x} \quad (4)$$

and

$$F = \frac{J}{C} + 2 \frac{k}{e} \frac{\partial \theta}{\partial x} \frac{V_1}{V_0} + \frac{k\theta}{e} \frac{\partial \log A}{\partial x} \quad (5)$$

where K and C are the thermal and electrical conductivities. We may then write (3) in the form

$$Q = \frac{J^2}{C} + J \left(\frac{k\theta}{e} \frac{\partial \log A}{\partial x} - \frac{2k\theta}{e} \frac{\partial}{\partial x} \frac{V_1}{V_0} \right) + \frac{\partial}{\partial x} \left(K \frac{\partial \theta}{\partial x} \right) \quad (6)$$

which for brevity we may put in the form

$$Q = Q_1 + Q_2 + Q_3 \quad (7)$$

so that the energy remaining in unit volume in unit time can be split up into three parts.

Of these the first part $Q_1 = \frac{J^2}{C}$ is simply the energy of the Joule heating effect.

The last term $Q_3 = \frac{\partial}{\partial x} \left(K \frac{\partial \theta}{\partial x} \right)$ gives the heat added by thermal conduction, whilst the middle term Q_2 corresponds to the Thomson effect, and if we write this in the form

$$-\mu J \frac{\partial \theta}{\partial x}$$

where μ is the Thomson coefficient, we have

$$\mu = \frac{2k\theta}{e} \frac{d}{d\theta} \frac{V_1}{V_0} - \frac{k\theta}{e} \frac{d \log A}{d\theta}$$

which for $A \gg 1$, i.e. complete degeneracy, gives

$$\mu = \frac{2\pi^2}{3} \frac{mk^2\theta}{eh^2} \left(\frac{8\pi}{3n} \right)^{2/3} \left\{ 1 - \frac{2}{3}\theta \frac{d \log n}{d\theta} \right\} \quad . \quad . \quad . \quad (8)$$

as compared with the older classical value,

$$\mu = \frac{3}{2} \frac{k}{e} \left\{ 1 - \frac{2}{3}\theta \frac{d \log n}{d\theta} \right\} \quad . \quad . \quad . \quad . \quad (9)$$

Strictly speaking equation (8) does not give the true value for the Thomson coefficient for the same reason that equation (9) was not entirely correct in the older theory (see p. 194), but slight differences of this kind are ignored in view of the numerous other approximations which have been made.

The equation (8) of the Sommerfeld theory gives very much smaller values than the classical equation (9) and is thus in much better agreement with the facts. In the case of silver, the value of μ according to equation (8) is about $\frac{1}{200}$ of that required by the older theory, and is roughly of the right order of magnitude.

In order to deal with the Peltier effect we consider a conducting wire kept at a constant temperature, but made of two different metals. In this case the last term of equations (6) and (7) will vanish, and we may to an approximation neglect the small Joule heating effect. If we then denote the factor by which J is multiplied in the second term by $-\Pi$, this will give the Peltier heat where

$$\Pi = \frac{k\theta}{e} \int_1^2 \left(\frac{2\partial}{\partial x} \cdot \frac{V_1}{V_0} - \frac{\partial \log A}{\partial x} \right) dx \quad . \quad . \quad . \quad (10)$$

the integration being carried out across the joint from metal 1 to metal 2. Under the usual assumption of the theory that $A \gg 1$,

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and that the free path is independent of velocity, the final value obtained for the Peltier effect is

$$\Pi = \frac{2\pi^2}{3} \frac{m(k\theta)^2}{eh^2} \left\{ \left(\frac{8\pi}{3n_2} \right)^{\frac{2}{3}} - \left(\frac{8\pi}{3n_1} \right)^{\frac{2}{3}} \right\} \quad . \quad . \quad . \quad (11)$$

Here again the equation for the Peltier Effect is not quite correct since, like the corresponding equation of the Lorentz theory, it ignores any possible transference of kinetic energy across the boundary between two metals owing to the difference between the fields of force surrounding the atoms. If these effects are ignored equation (10) requires the Peltier coefficient Π to be proportional to θ^2 , whereas the older theory required Π to vary directly as the absolute temperature. Actually, however, neither prediction is confirmed experimentally when the data are surveyed as a whole, although the Sommerfeld equation gives results of the right order of magnitude.

By combining these two methods we can obtain an expression for the thermo-electric force of a circuit of two metals, subject to the same two simplifying assumptions, that the free path is independent of the velocity, and that we ignore effects due to the differences between the fields of force round the atoms in the two metals. In this way the equation for the E.M.F. of an electric couple with junctions at θ' and θ'' is deduced as

$$E_T = \frac{\pi^2}{3} \frac{mk^2}{eh^2} \left\{ \left(\frac{8\pi}{3n_1} \right)^{\frac{2}{3}} - \left(\frac{8\pi}{3n_2} \right)^{\frac{2}{3}} \right\} (\theta''^2 - \theta'^2) \quad . \quad . \quad (12)$$

so that E_T is proportional to $(\theta''^2 - \theta'^2)$ whereas the older classical methods required E_T to be proportional to $(\theta'' - \theta')$. If we denote by t , the difference between $(\theta'' - \theta')$, the Sommerfeld relation may be written in the form

$$\begin{aligned} E_T &= C(\theta''^2 - \theta'^2) = C(\theta'' + \theta')(\theta'' - \theta') \\ &= Ct(2\theta' + t) \end{aligned}$$

and a relation of this type is in somewhat better agreement with the facts than the variation with $(\theta'' - \theta')$ predicted by the older theory. But the data as a whole are not in agreement with a simple proportionality between E_T and $(\theta''^2 - \theta'^2)$. In the case of the couple silver-sodium, the value of E_T calculated from equation (12) is of the order 2 micro-volts per degree centigrade at 0°C ., which is somewhat less than the observed value, but is of the right order of magnitude.

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7. Emission Phenomena

(a) *Thermionic Emission.*

The new electron theories have attained their greatest success in connexion with the emission phenomena, the chief work being due to L. Nordheim and R. H. Fowler, although preliminary investigations were made by Sommerfeld and Houston. In the chapter dealing with the older Lorentz theory, we have already seen how the equations for the thermionic emission current were obtained by considering the equilibrium between the electrons inside the metal, and those in the surrounding space, and we have noted the difficulties which were met with on account of the specific heats, and the question of electron reflection. Taken as a whole, it may be said that the applications of the new theories fall into two classes. On the one hand the conception of an equilibrium between the electrons inside a metal and those in the surrounding space was considered from the point of view of the new statistics, and here, since the new theories require the specific heat of the internal electrons to be almost zero, the results led to an equation of the type $I = A\theta^2 e^{B/\theta}$. On the other hand, the ideas resulting from the wave theory have been used to investigate the problem of the penetration of the surface of a metal by an electron, and this has led to the calculation of the reflection coefficient, and to an understanding of the effects of surface films.

If we are to consider the process of emission from this point of view, we require to know two factors. The first is the number of electrons which strike the surface of the metal from within in unit time per unit area, and the second is the fraction of these electrons which are emitted. In the general line of argument adopted by Nordheim and Fowler, the electrons are considered to move freely within the body of the metal in accordance with the Sommerfeld theory, and then to encounter a more or less abrupt change of potential when they pass through the surface layer. It can then be shown that, to a first approximation, we need only consider the component of the electron's velocity at right angles to the surface, so that the problem becomes one of the passage of wave trains (representing the electrons) through the changes of potential which occur at the surface. In accordance with the nomenclature of Nordheim¹ we may call the number of electrons incident from within on a surface of unit area per unit time with kinetic energy W normal to the surface,

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 $N(W)$, and the fraction transmitted $D(W)$. The total emission current is then clearly given by

$$I = e \int_0^\infty N(W) D(W) \cdot dW,$$

and the problem consists in finding $N(W)$ and $D(W)$. For the first of these, the application of the Sommerfeld theory leads directly to the relation

$$N(W)dW = \frac{4\pi m}{h^3} k\theta \log(1 + e^{-(W-\mu)/k\theta}) dW$$

where μ is the parameter equivalent to the thermodynamic partial potential of an electron. The emission current is therefore given in general by

$$I = \frac{4\pi m e}{h^3} k\theta \int_0^\infty D(W) \log(1 + e^{-(W-\mu)/k\theta}) dW.$$

We have now to consider the factors affecting $D(W)$, and for this purpose it is necessary to simplify the condition of affairs at the surface. In the original paper of Nordheim,¹ it was assumed that there was a definite potential difference C between the electron inside and outside the metal, so that in the passage of an electron through the boundary, the potential underwent a change of the form shown in Fig. 52, where the ordinates represent potential, and the abscissae the distance of the electron from the surface; in order to simplify the calculations, this type of curve may be reduced to that shown in Fig. 53. During the passage of the electron through the surface its kinetic energy is reduced by an amount C , and according to the older classical or 'particle' theory, we should expect the electron to escape if W were greater than C , and to remain within the metal if W were less than C , so that we should have $D(W) = 0$ for $W < C$, and $D(W) = 1$ for $W > C$. According to the new wave theories, however, the change is not so sharp, and whilst the electron is still unable to escape if W is less than C , the value of $D(W)$ is given by $D(W) = \frac{4[(W-C)W]^\frac{1}{2}}{[W^\frac{1}{2} + (W-C)^\frac{1}{2}]^2}$ when W is greater than C . Since only the electrons for which W is greater than C are able to escape, the expression for the emission current is

$$I = \frac{4\pi m e}{h^3} k\theta \int_C^\infty D(W) \log(1 + e^{-(W-\mu)/k\theta}) dW$$

which leads to the relation

$$I = \frac{4\pi m e k^2}{h^3} \bar{n} A^2 e^{-\frac{C-\mu}{k\theta}}$$

where \bar{D} is a mean transmission coefficient for those electrons which are able to escape, i.e. those for which $W > C$. For the single step in potential assumed in Fig. 53, it was shown by Nordheim¹ that the value of \bar{D} was about 0.5, so that the expression for the emission current is of the form $I =$

where $A = \frac{h^3}{4\pi m^2 e} = 60$ (approximately).

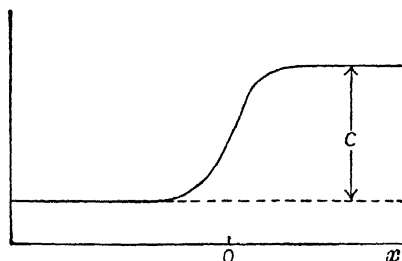


FIG. 52.

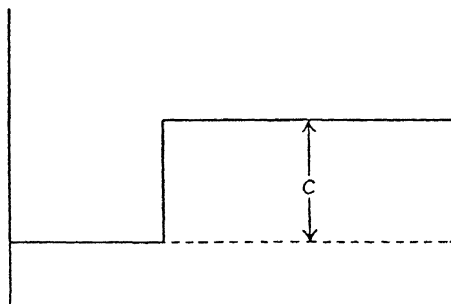


FIG. 53.

This is in remarkable agreement with the facts, but later investigation has shown that this is to some extent fortuitous, and is not strictly correct. The reason for this is that the type of boundary surface assumed in Fig. 53 is too simple, and neglects in the first place the effect of the image potential due to the electron as it moves away from the surface. This image potential is equal to $-e^2/4x$ where x is the distance from the surface, and, when this is taken into account, the field at the surface is of the form shown in Fig. 54. The calculation of $D(W)$ for this kind of a surface has been carried out by Nordheim,² and in this case it is found that the mean transmission coefficient \bar{D} instead

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of being about $\frac{1}{2}$ is very nearly unity, so that the equation becomes much more nearly

$$I = \frac{4\pi me k^2}{h^3} \theta^2 e^{\frac{(C-\mu)}{h\theta}}$$

and the theoretical value of the constant A is about 120 instead of the usually accepted value of 60, but in view of the unsatisfactory nature of these equations for comparison with the facts, it is considered that it is sufficient to have obtained the right order of magnitude. On the other hand there is a serious discrepancy between the theoretical value of A , and the results of DuBridge for metals such as platinum, which we referred to in Chapter VII, since here the experimental values of A are 50 or 100 times too

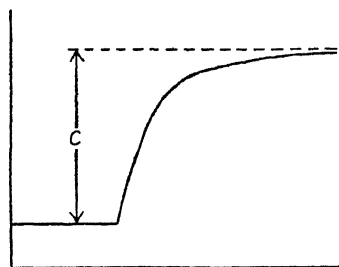


FIG. 54.

large. These difficulties have been discussed in detail by R. H. Fowler,³ but the position is still obscure. One possible explanation is that the actual emitting surface is very much greater than that measured from the dimensions of the electrode, since differences of this kind have been met with in connexion with the over-potential of platinum electrodes. But it is doubtful whether this can account for the whole effect,

and it is probable that the identification of χ in the thermionic equation, with the $(C-\mu)$ of the theoretical equation is not justified, but that more properly $C-\mu = \chi_0 - \alpha\theta$, in which case the value of A determined from the observations is equal to $120 \times e^{\alpha/h}$. These variations in the work function may be due to a slight loosening of the lattice at high temperatures, and to variations in the number of free electrons. A further possibility is a temperature variation of $D(W)$, so that a number of hypotheses can be suggested.

In the above description we have referred to the passage of an electron through a surface which can be represented by a simple step in potential, but if anything in the nature of a surface film be present, we may expect the change to be accompanied by a variation of the type shown in Fig. 55, the effect of an electro-positive surface film being to reduce the final work of emission C , but to create a potential ridge B of much the same height as the value of C for the pure metal. For purposes of calculation

this may be simplified to the form shown in Fig. 56. The transmission coefficients for electrons penetrating potential ridges of this kind have been investigated by Nordheim² and Fowler,³ and it is here that the wave conceptions differ from those of the older classical theories. According to the older 'particle' theories an electron could only penetrate a potential ridge such as that shown in Fig. 55, if its kinetic energy W were greater than B . But

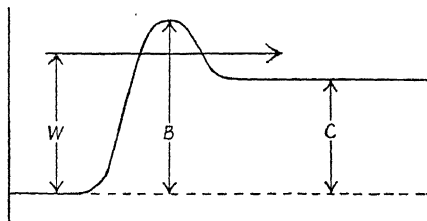


FIG. 55.

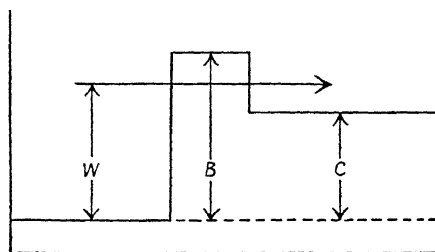


FIG. 56.

according to the new wave mechanics, an electron can penetrate a thin ridge, and electrons can escape as long as W is greater than C , provided that the ridge, representing the surface layer, is not too thick. The value of $D(W)$ for a ridge of this type was first calculated by Nordheim,¹ and later corrected by Fowler,³ and if we plot $D(W)$ against W , the curve obtained is of the type shown in Fig. 57, and Fig. 58 shows the relation of curves of this type to those for the pure metal. In this case the value of C for the pure metal is 10 volts, and the surface film reduces this to 8 volts, whilst forming a ridge B of height 10 volts, and of thickness shown by the figures on the different curves. Since the interpretation of these curves leads to a discussion of the secondary effects due to surface films, we shall not deal with

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the matter further, but it is interesting to note that, as shown by Fowler,³ they indicate that if a surface film be formed on a metal, the emission will still be given by an equation of the type

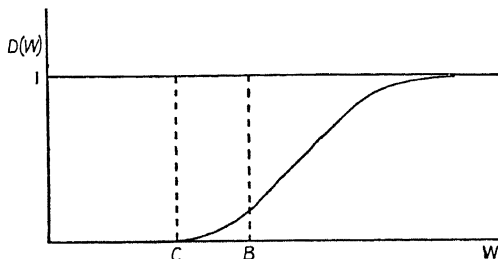


FIG. 57.

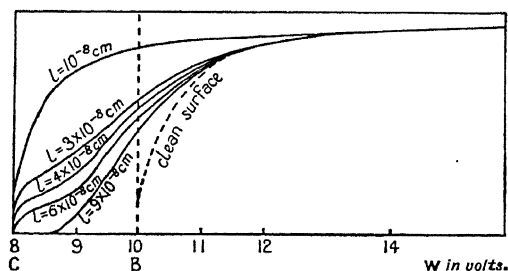


FIG. 58.

$I = A\theta^2 e^{-\chi/\theta}$, but with reduced values of A and χ , the mutual changes of A and χ being of such a nature that

$$\log A = \xi - \eta(B - C)$$

where ξ and η are constants, and $(B - C)$ is the reduction in χ due to the surface layer. Actually it has been shown by DuBridge⁴ that a relation of this kind is in good agreement with the facts.

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4. DuBridge. *Phys. Rev.* 1928, **31**, 236.

(b) *Strong Field Emission.*

The Sommerfeld theory has been applied to the problem of strong field emission by R. H. Fowler and his collaborators, whilst further investigations are due to Houston,¹ and Waterman.² In

the work of Fowler and Nordheim³ the subject is again treated as a one-dimensional problem involving only the kinetic energy (W) of the electron normal to the surface, and the emission coefficients are calculated when an external electric field acts so that the potential energy of the electrons varies as shown in Fig. 59, the sloping line representing the effect of the external field.

As in the thermionic theory we should, strictly speaking, include the image effect, which results in a rounding-off of the sharp corner at the top, but it can be shown that this effect is negligible at ordinary temperatures. As before we may write (DW) for the fraction of the electrons with energy W which penetrate the

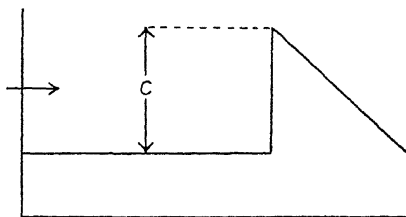


FIG. 59.

potential peak of the type shown in Fig. 59, under the influence of the external field F . The analysis then shows that

$$D(W) =$$

where $\kappa = 8\pi^2 m/h^2$. The total number, $N(W)$, of electrons reaching the surface per unit area per unit time with energy W normal to the surface is given by the same expression as that used in the thermionic theory, and in this way the equation for the strong field emission is deduced as

$$\begin{aligned} I &= \frac{16\pi me}{Ch^3} \int_0^\mu W^{\frac{1}{2}} (C-W)^{\frac{1}{2}} (\mu-W) e^{-4\kappa(C-W)^{\frac{1}{2}}/3F} dW \\ &= \frac{e}{2\pi h} \frac{\mu^{\frac{3}{2}}}{(\chi+\mu)\chi^{\frac{1}{2}}} F^2 e^{-4\kappa\chi^{\frac{1}{2}}/3F} \\ &= 6.2 \times 10^{-6} \frac{\mu^{\frac{3}{2}}}{(\chi+\mu)\chi^{\frac{1}{2}}} F^2 e^{-6.8 \times 10^7 \chi^{\frac{1}{2}}/F} \quad \dots \quad (2)^* \end{aligned}$$

where $\chi = C - \mu$, and is the thermionic work function.

* In the original paper there is a misprint, and -2.1×10^8 is given instead of the correct value -6.8×10^7 in equation (2).

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This equation is thus of the general type $I = CF^2e^{-\alpha/F}$, and is almost indistinguishable from the experimental equation $I = Ce^{-\alpha/F}$ to which we referred in Chapter VII. For the majority of metals the value of $\chi^{3/2}$ is of the order 10, so that the emission should begin to be sensible for fields of the order 10^7 volts/cm., whereas the experiments indicate an appreciable emission for values of F of about 10^6 volts/cm. This difference is ascribed by Fowler and Nordheim to the presence of surface irregularities or peaks giving higher values of F than that calculated from the dimensions of the apparatus. The equation of Fowler and Nordheim refers strictly to the absolute zero of temperature, but it can readily be shown that the results are independent of tem-

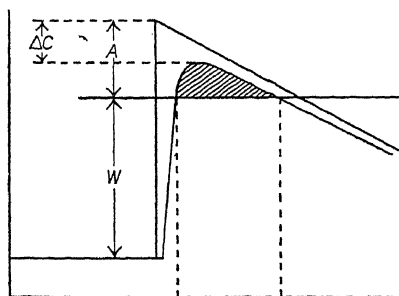


FIG. 60.

perature at all ordinary temperatures, and this point has been discussed by Houston,¹ and also by Fowler and his collaborators.

In a later paper Nordheim⁴ has investigated the problem for the more accurate type of boundary shown in Fig. 60, and the result is a slight decrease in the field strength necessary to cause emission as compared with the simplified boundary assumed in Fig. 59. But this difference is not sufficient to reduce the coefficient of $1/F$ to the observed values, so that the existence of surface irregularities or sensitive spots has again to be assumed.

In a later paper, Stern, Gossling, and Fowler⁵ have discussed in detail the factors which have to be taken into account before the equation (2) can be compared directly with the experimental data. The quantities which are actually measured are the total current passing between the electrodes, and the applied voltage, whereas the equation refers to the current density, and the surface field. It can be shown that the effects of space charge are in general negligible, so that the surface field is proportional to the

measured voltage, the proportionality factor being determined by the shape and dimensions of the apparatus. If the emitting area be constant, the current and current density will be proportional, and since the experimental data agree with a relation of the type $I = CF^2e^{-\alpha/F}$, the equation may be used to estimate the size of the emitting area. For one or two tungsten wires which had been pointed and polished by electrolytic action, the emitting area was found to be of the same order as the area of the point, but in general the emitting area is very much smaller, the estimated values ranging from 10^{-8} cm.² to 10^{-13} cm.², although the smallest of these values may be underestimated owing to the effects of surface films. The effect of films of electro-positive metals such as the alkalis and alkaline earths upon the emission from tungsten was also examined in detail, and the theoretical conclusions were found to be in general agreement with the facts, but as these are essentially secondary phenomena, we shall not discuss them further.

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8. General Discussion

In discussing the position of the theories based on the new quantum mechanics, it is necessary to distinguish rather sharply between the original restored 'electron gas' theory of Sommerfeld, and the later modifications due to Houston, Bloch, Nordheim, and others. Apart from the fact that it was obviously of too simple a nature, the original theory of Sommerfeld was open to the criticism that the collision processes were not treated entirely correctly. In the general method of Lorentz and Sommerfeld, there is no objection to considering the electric force as producing a slight displacement of the distribution function, since we may quite justifiably expect the external field to produce a slight displacement of the energy states, just as, for example, the spectral lines are displaced in the Stark Effect (the displacement of spectral lines by an electric field). But the collision processes have to be treated differently in the old and the new methods, for whereas the old statistics placed no restrictions upon the collisions, the new methods only allow an electron to be scattered

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into a state which is unoccupied. These difficulties have been discussed by Nordheim,¹ who has shown that the Sommerfeld treatment is justified only if the scattering system of atoms is not influenced appreciably by interaction with the electrons, and this is of course the assumption made in all the older theories, which regarded the atoms as immovable on account of their relatively great mass. If this assumption is accepted, the additional terms due to the use of the new statistics are found to cancel out, so that the Sommerfeld treatment is in effect justified, although as we have shown in (4) and (5) above, the more complete examination of Houston and Bloch shows that the collisions really involve a transference of energy, equal to $h\nu$, between the electron and the atom.

We have already noted (p. 268) that the Sommerfeld equations are unsatisfactory as regards the variation of the resistance with temperature, but, apart from this, very great confusion was caused by the long free paths, which the theory requires to be several hundred times the inter-atomic distance at room temperature. In the Lorentz-Sommerfeld treatment the free path term λ is an abbreviation for $\frac{1}{\pi n R^2}$ (see p. 267), and the critics of the theory quite reasonably objected that it had always been considered unjustifiable to unite free paths of this magnitude with the simple 'gas' type of calculation. On the other hand the supporters of the theory pointed out that long free paths were indicated by many facts, such as the marked increase in resistance produced by small amounts of impurity. Actually both these points of view were to some extent justified. The fact that the new statistics indicated long free paths could quite reasonably be taken as indicating that the general viewpoint might be correct, but, on the other hand, the critics of the theory were entirely justified in maintaining that the Lorentz type of argument was strictly logically inadmissible with such long free paths, or such very small values of R . As we have already explained, the replacement of the atom by a minute sphere is merely a mathematical device for estimating the scattering effect, and the minute values of R necessary to give the correct value for the conductivity have no real physical meaning.

The Sommerfeld theory thus occupies a very curious position. From one point of view, the critic could maintain logically that it failed to solve the conductivity problem for the reasons which we have just described. On the other hand, the supporter of the

theory could maintain equally well that the precise conceptions of the Lorentz treatment were only drawn upon in order to obtain a rough estimate of the scattering effect, and that the general order of magnitude was correct. It became increasingly apparent, however, that a treatment which completely ignored the effects of the atoms was much too simple in nature, so that the real value of the Sommerfeld theory lay, not so much in providing a solution of the conductivity problem, as in indicating that an electron gas obeying the Fermi-Dirac statistics would have properties entirely different from those of the electron gas of the classical theory. The new theory showed further that the correct order of magnitude could still be obtained for the Wiedemann-Franz ratio, and that it was possible to overcome many of the older difficulties in connexion with the thermo-electric and emission phenomena. The Sommerfeld theory was thus of vital importance in introducing a new method of approach to the electron theory of metals, and although the original theory was much too simple, and was open to criticism from several points of view, it is of supreme interest as marking the beginning of an entirely new line of thought.

As regards its agreement with facts, the Sommerfeld theory gives a general account of the electrical properties, except in connexion with supra-conductivity, and variations in the Wiedemann-Franz ratio. Like most of the earlier theories, the Sommerfeld theory is quite unable to account for the sudden appearance of supra-conductivity at a definite temperature, especially as no discontinuity in the thermal conductivity is found. Any variation in the Wiedemann-Franz ratio from one metal to another,* or in any one metal under pressure, tension, &c., or in different directions in a single crystal, is in contradiction to the Sommerfeld theory which requires the λ terms to cancel out when the ratio of the conductivities is taken.

The original Sommerfeld theory was not in agreement with the variation in conductivity with direction in a non-cubic crystal, but the later developments of Houston and Bloch remove this difficulty. Considered quantitatively, however, the method of Houston is not entirely satisfactory, for, although the consideration of the electron as a wave packet, and the use of the Debye-Waller equation give a satisfactory explanation of the long free

* We refer here of course to the true Wiedemann-Franz ratio referring to the metallic part of the thermal conductivity, and not the ordinarily observed ratio referring to the total thermal conductivity. (See p. 77.)

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path, it appears rather arbitrary to combine this conception with the equations deduced by the Lorentz-Sommerfeld method in which the outlook is so very different. The only justification for this lies in assuming that, whilst the Debye-Waller formula gives the probability of a collision occurring between an electron and an atom, the resulting deflexion, since it cannot be calculated directly from quantum theory, may be taken as of the same order as that given by the method of spheres used in the Lorentz-Sommerfeld treatment. The method is therefore approximate only, and the detailed comparison of the figures should not be made. The early methods of Houston were also criticized by Brillouin² on the grounds that the Debye-Waller equation was deduced for light quanta obeying the Einstein-Bose statistics, whilst the electrons are assumed to follow the Fermi-Dirac Law. As was pointed out by Bloch,¹ the later method of Houston appears unsatisfactory since the statistical treatment is incomplete.

From the point of view of electrical conductivity, the most complete investigation is undoubtedly that of Bloch, since this treats the interaction of the electrons with the lattice as a whole. The theory is, however, open to the criticism that the mutual interaction of the electrons is not considered, and this work has therefore been criticized on the grounds that it ignores factors which are probably quite as important as those taken into account. The method of Bloch involves the assumption that in considering the motion of any one free electron, the remaining free electrons may be regarded as smoothed out, or distributed uniformly throughout the crystal, so that the particular electron considered moves in a strictly periodic field. It is therefore incorrect to say that the remaining free electrons are completely ignored, since the conception of one free electron moving among a number of positive ions with nothing to counteract their positive charges would clearly be unjustified. But, although constituting a great advance upon the original 'gas' theory, the assumptions of the Bloch theory are still but approximations for the mutual repulsion of the electrons is not sufficiently taken into account, and there is some justification for the criticism that the mathematical analysis has been elaborated to a degree which is unjustified in view of the simplifying assumptions which are involved.

The final solution of the problem will thus have to take into account both the mutual effect of the electrons, and of their interaction with the ions, and for the present the mathematical difficulties have proved too great, but in this connexion we may

refer to the paper by Lennard-Jones³ in which the matter is further discussed. This author, after criticizing the Sommerfeld theory, discusses the distribution of the free electrons in a metal crystal on the assumption that the electrons obey the Fermi-Dirac statistics, and that the potential field due to the ions is triply periodic. A complete solution for a three dimensional crystal is not obtained, and the problem is therefore simplified to that of a hypothetical two dimensional metal in which the nuclei are replaced by a series of parallel line charges arranged so as to intersect a plane perpendicular to them in square array. A section of this system is then taken between two planes at a distance d (of atomic dimensions). The charge on each line charge within the distance d is taken to be Ze , and the number of the electrons in the volume considered is sufficient to make the system as a whole neutral. Under these conditions the potential will be constant along lines parallel to the line charges, but will vary periodically in planes at right angles to the line charges.

A typical solution of a problem of this type is shown in Fig. 61, the nuclei (represented by the intersection of the line charges with the plane of the paper) being shown by crosses. The dotted lines represent lines of equal potential, and near a nucleus they are circles, but, as the distance from the nucleus increases, the equipotential lines are deformed until a critical curve is reached which is shown by a continuous line. This curve extends throughout the whole crystal, and encloses another system of closed curves surrounding the centres of the squares. These same curves also indicate the probable electron density in the metal, and this is much greater in the middle of the squares formed by the nuclei than in other regions. The electrons within these second systems of closed curves may be regarded as shared between the four surrounding nuclei, since they cannot be definitely associated with any one nucleus, and these shared electrons form a lattice which penetrates that of the nuclei. From this it can be seen that the picture presented is in some ways very like that of the lattice theory of Lindemann, but it differs from this in that the electron lattice is not necessarily static even at the absolute zero of temperature. For since the method assumes the Fermi-Dirac statistics, the electrons retain a high energy at all temperatures, and those which have sufficient energy may reach the equipotential lines, and may then travel from one end of the crystal to another as long as the field is strictly periodic. There may thus

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be a continual interchange of electrons from one part of the metal to another, in spite of the fact that the probable electron density in one of the shared regions is always greater than that elsewhere.

The new theories are thus still far from providing a complete solution to the conductivity problem, and their chief success is

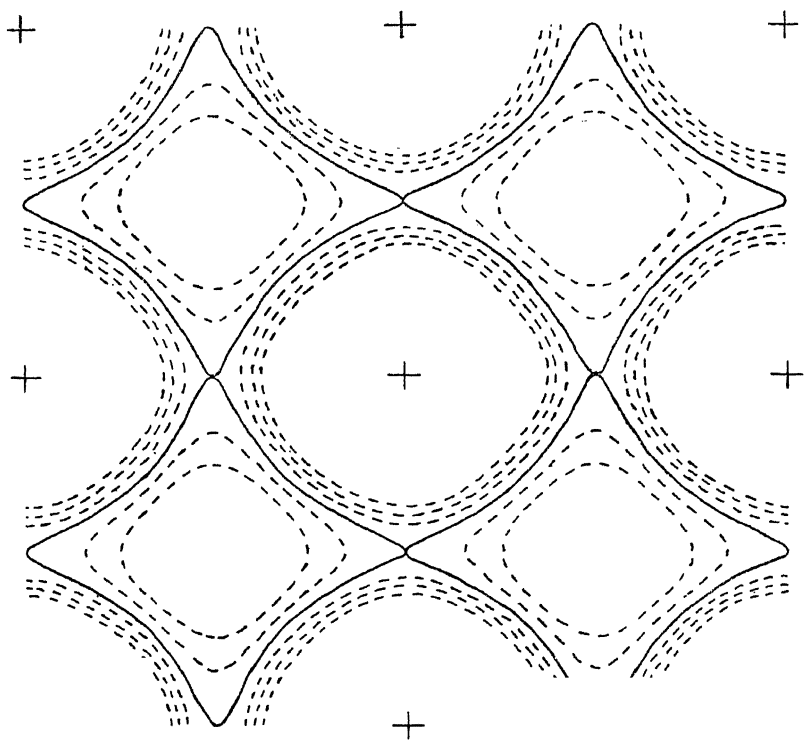


FIG. 61

undoubtedly in connexion with the emission phenomena. The old difficulties in connexion with the sharpness of the photo-electric threshold frequency, and the temperature independence of the photo-electric and strong field emission are satisfactorily removed, and all three types of emission come under one general explanation which is strikingly supported by the application of the wave methods to the problem of the passage of electrons through surface films. The general conception of conducting electrons of high energy required by the Fermi-Dirac

statistics is also confirmed by the experiments of Davisson and Germer on the scattering of electrons, since these indicated differences of the order 10 electron volts between the internal and external electrons. At the same time it must not be forgotten that the emission equations are of a type which cannot be tested critically, and that there is a serious discrepancy between the theoretical value (120) for the equation $I = A\theta^2 e^{x/\theta}$, and the experimental values for metals such as platinum.

In this connexion it is most unfortunate that few direct tests of the new statistical methods can be made, since it is only at very low temperatures that ordinary gases become appreciably degraded. One exception is the application by R. H. Fowler of the new methods to the problem of the white dwarf stars such as the companion of Sirius, where the density is of the order 10^5 grams per cubic centimetre, and can only be accounted for if the energy is great enough to ionize the atoms to such a degree that they are stripped of all their outer electrons. Here the Fermi-Dirac statistics permit a very high energy even at the absolute zero of temperature, and this enables the great density to be reconciled with the radiation data, but the explanation is general, and qualitative rather than exact.

Apart from this, the new methods have been tested only in the case of the electron theory of metals, and the position is thus logically very unsatisfactory, since we can only test the theory in a case where we have to assume the very thing about which we are uncertain, namely whether the conducting electrons in a metal can legitimately be treated as particles of a gas.

We have already noted that the Fermi-Dirac statistics enabled Pauli to give the first explanation of the magnetic susceptibility of the alkali metals. In this work, the small value of the susceptibility is regarded as due to the completely degraded state of the electron gas, in which two electrons of equal and opposite magnetic momentum occupy all the cells of the momentum space nearest the origin, so that the pairs in each fully occupied cell make no contribution to the susceptibility. In this way Pauli obtained values which agreed approximately with the observed susceptibilities. It has, however, been pointed out by Bieler that no correction was made for the diamagnetic contribution of the ions, and that, when this is taken into account, the theoretical estimates are lowered, and actually lead us to expect potassium, rubidium, and caesium to be diamagnetic, so that the confirmation is again of an approximate nature only.

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The Sommerfeld theory and its later modifications are thus in a peculiarly interesting position. They indicate clearly that the old ideas of bullet-like electrons possessing energies given by the simple kinetic theory, and colliding with large spherical atoms, are essentially unsound, and must be replaced by the newer conceptions of the wave mechanics. They suggest that the applications of the Fermi-Dirac statistics will remove many of the difficulties of the older theories. But the quantitative methods are at present unsatisfactory, and incomplete, for the original Sommerfeld theory is certainly too simple, and is open to the objections to which we have referred above, whilst the later developments, in spite of all their mathematical ingenuity, can hardly escape the criticism that the mathematical development has been carried further than is justified by the simplifying assumptions which are involved.

If the reader asks, here, what kind of a 'picture' of a metal is given by the new theories, it is extremely difficult to give any really detailed answer, and it is indeed rather the essence of the new theories that we must no longer attempt to form any precise mechanical pictures of events on an atomic scale. We may perhaps best conceive of the crystal of a metal as one huge molecule, in which the valency electrons occupy a whole series of energy levels. That is to say, just as, on an infinitely smaller scale, a hydrogen molecule contains two positive ions, and two valency electrons, with the possibility of continual interchange between the two, so we may look upon a metallic crystal as consisting of an immense number of positive ions, which give rise to a corresponding number of electrons distributed over a whole range of energy levels, but with the continual possibility of interchange. If we accept the Fermi-Dirac statistics, the energy distribution curve for the free electrons is of such a nature that at ordinary temperatures the distribution is but little affected by temperature, the greater number of the electrons occupying the cells nearest the origin in the momentum diagram of Fig. 49, and only a few having velocities which exceed the critical value. But if we accept the general viewpoint of Houston, Bloch, and Lennard-Jones, it is just these few electrons with the highest velocities which are chiefly concerned in the conductivity and emission processes. From some points of view, therefore, there is a curious resemblance between the conclusions of the new theory, and of the older theories which postulated few electrons and long free paths, or of the Dual Theory of E. H. Hall which imagined a small

number of 'free' electrons in equilibrium with a much larger number of associated electrons. But the resemblance is general, and qualitative rather than exact. For the older theories required the mean square velocity of the free electrons to vary as the square root of the absolute temperature, which is not in agreement with the new statistics, whilst, apart from this, the crude attempts of the older theories to give precise mechanical pictures to the individual processes are quite unjustified.

It can be seen therefore that the new theories in some ways express the same ideas as those suggested by the older theories, although the quantitative details and the general viewpoint are profoundly different. The Sommerfeld theory began as a free electron theory expressing the same ideas as those of Lorentz, but with a different distribution law. In the hands of Houston and Bloch it may be said to have amplified the theory of Wien and Grüneisen, but to have overcome the difficulties which the Wien theory encountered on account of its assumption of an absolutely constant electron velocity. The same work together with that of Lennard-Jones emphasizes the importance of the comparatively few electrons with high velocities, and thus amplifies the ideas of the older theories of E. H. Hall and others, which postulated the existence of a small number of conducting electrons. Whilst if the views of Lennard-Jones be accepted, the complete solution of the problem, when the interaction both of the electrons and of the ions is taken into account, may lead to a conception which has many features similar to that of the electron lattice theory of Lindemann.

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CONCLUSION

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1. The Periodic Classification

BEFORE concluding this review of the electrical and thermal properties of metals, and of the various electronic theories which have been suggested in order to account for these properties, we shall refer briefly to evidence from one or two other directions which bears essentially upon the same problem. For this purpose it is necessary to have a clear understanding of the Periodic Table of the elements, and of its interpretation according to modern theories of atomic structure. In Fig. 62 we reproduce the usually accepted form of the Periodic Table, the letters referring to the chemical symbols of the elements, whilst the figures under each element give the so-called *atomic numbers*, which, for the present, we may consider simply as giving the numbers which the elements occupy in the sequence. We shall assume further that the reader has a sufficient knowledge of the elementary facts of chemistry to understand the meaning of this table, and the general valency relations which are shown by the different families of elements in their chemical reactions.*

The general periodic table of the elements was made by Mendeléeff as long ago as 1869, but its interpretation in terms of atomic structure is comparatively recent. The work of Rutherford, Soddy, Moseley, Russell, Fajans, and others, led gradually to the present conception of a nuclear atom, consisting of a minute positively charged nucleus surrounded by a sufficient number of electrons to keep the atom as a whole neutral. The dimensions of the nucleus are of the order 10^{-12} cm., whilst the zone occupied by the surrounding electrons is of the order 10^{-8} cm. The charge on the nucleus is equal to $+Ze$, where $-e$ is the charge on one electron, and Z is a whole number, the so-called *atomic number*, which gives the position of the element in

* The reader who is in doubt upon these points may well consult a book such as Sidgwick's *Electronic Theory of Valency*, whilst many modern text books of chemistry give general reviews of the subject.

the Periodic Table. Since the atom as a whole is neutral, an atom with atomic number Z is surrounded by Z electrons. Thus

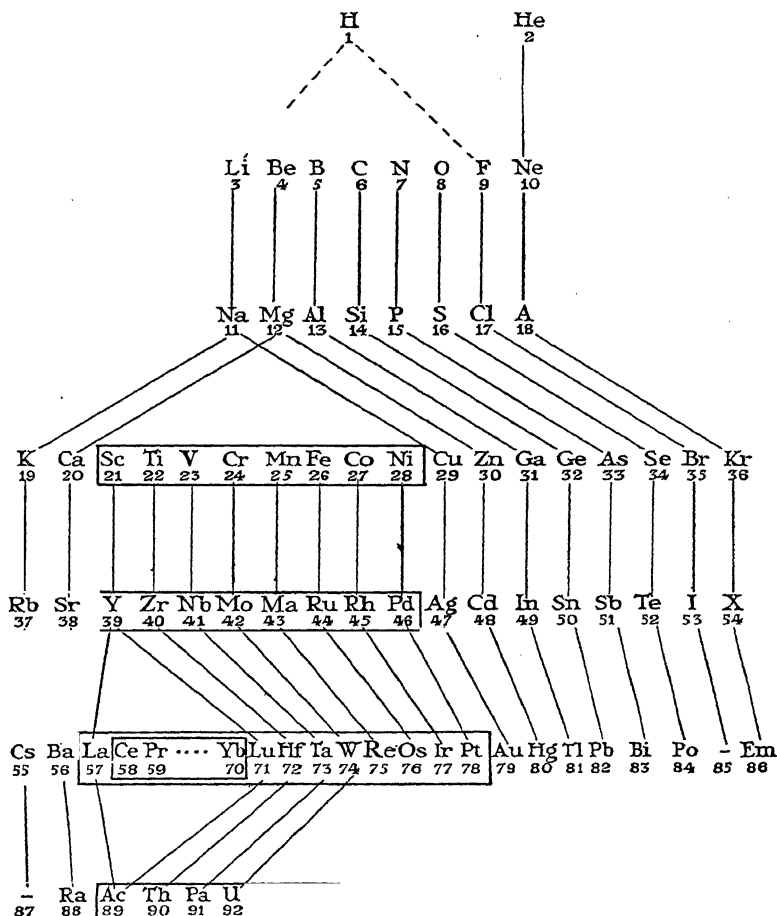


FIG. 62.

in aluminium ($Z = 13$), the nucleus has a charge of $+13e$, and is surrounded by 13 electrons.

In the original Bohr theory the electrons are imagined to revolve round the nucleus in elliptical orbits so that the centrifugal force balances the electrostatic attraction, but whereas the older classical mechanics would have allowed an infinite number of

such orbits, the Bohr theory postulates that only certain orbits or *stationary states* are possible, and these are characterized by the fact that the angular momentum of an electron in the different states is always an integral multiple of $\frac{h}{2\pi}$. In the simple Bohr theory the states are characterized by two quantum numbers. Of these the principal quantum number n is a measure of the energy of the orbit, and may be considered roughly as representing the major axis of the ellipse, whilst the secondary quantum number k may be considered to a rough approximation as representing the latus rectum, and hence as a measure of the excentricity. The problem of atomic structure* then consists in finding how the electrons in the different atoms are divided into groups characterized by the principal and subsidiary quantum numbers. The later developments of the theory have shown that more than two quantum numbers are required in order completely to define the electron orbits, whilst apart from this the new quantum mechanics indicate that the original crude mechanical picture of electrons moving in elliptical or disk-like orbits is incorrect, and must be replaced by the conceptions of the wave mechanics. In this way the principal quantum number of the Bohr theory is still retained, and is a measure of the energy of the electron in the orbit concerned, but as we have already briefly mentioned in our account of the Pauli principle, an electron state is now characterized by four quantum numbers. For our present purpose it is sufficient to deal with the simple classification into groups and sub-groups, and the following Table† gives the accepted electronic structures for the free atoms of the different elements. The secondary quantum number l used here is that of the Pauli notation and corresponds to $(k-1)$ of the older Bohr theory. From this table it can be seen that the regular sequence in the Periodic Table is due to the building up of the successive groups or shells of electrons. It will further be noted that the group of 2 electrons in the 1 quantum shell, and of 8 electrons in the shells of higher quantum number, form stable configurations, and that the

* Space does not permit any detailed account of recent theories of atomic structure to be given here, and the reader who is in need of further details should consult books such as Sidgwick, *The Electronic Theory of Valency*; Andrade, *The Structure of the Atom*.

† This table is constructed from that given by Dr. N. V. Sidgwick, F.R.S., in his book on *The Electronic Theory of Valency*, and I must express my thanks for permission to do this.

inert gases are characterized by having one of these stable groups for their outermost shell of electrons. The transitional elements in the long periods are the result of the fact that, for quantum shells for which n is greater than 2, groups of 8 electrons have a provisional stability but later expand into a group of 18. Finally the Rare Earth group of elements corresponds to the stage at which the group of 18 electrons in the 4 quantum shell is expanding into one of 32. It can be seen that whenever we have an element with one electron outside a group of 8 or 18, the corresponding metals (the alkalis, and metals of the copper group) have a very high conductivity per atom. From our point of view the important thing to note is the way in which a group of 8 electrons is built up, and it will be seen that this takes place in such a way that the 8 electrons are not exactly equivalent, but fall into two sub-groups of 2 and 6 electrons respectively. In the case of lead, for example, all four valency electrons are in the 6 quantum shell (i.e. the group of electrons for which $n = 6$), but the four are not exactly equivalent as regards their energy, two being in the sub-group characterized by the quantum numbers 6_0 , and two in that denoted 6_1 . As we shall see later, the formation of this sub-group of 2 electrons is of vital importance, since, in some cases, the stability of the sub-group is so great that it persists in the solid metal. In the same way, in a shell of 18 electrons, there are sub-groups of 2, 6, and 10 electrons respectively.

It must be understood that these are the structures of the free atoms, and that the numbers of the outermost or valency electrons are not always exactly the same in the case of the solid metals. Thus in the case of titanium, the free atom in the normal state has two valency electrons in the outermost 4 quantum shell, and ten electrons in the next 3 quantum shell, but, as we shall see in the next section, it is almost certain that in the solid crystal of titanium, each atom has only eight electrons in the 3 quantum shell, and has thus four valency electrons. In the same way the free atom of palladium contains no valency electrons, the outermost shell consisting of a completed group of 18, whereas in nickel and platinum there are two valency electrons surrounding a shell of 16. But in the solid state it is probable that all the three elements, nickel, palladium, and platinum, are similar as regards the number of electrons in the valency shell. These relations are however but imperfectly known for the solid state, the only real evidence being that from the crystal structures which we shall describe in the next section.

ATOMIC STRUCTURES

<i>Element and Atomic Number.</i>	<i>Principal and Secondary Quantum Numbers.</i>									
	n = 1	2	3	4						
	l = 0	0 1	0 1 2	0 1 2 3						
1 H	1									
2 He	2									
3 Li	2	1								
4 Be	2	2								
5 B	2	2	1							
6 C	2	2	2							
7 N	2	2	3							
8 O	2	2	4							
9 F	2	2	5							
10 Ne	2	2	6							
11 Na	2	2	6	1						
12 Mg	2	2	6	2						
13 Al	2	2	6	2	1					
14 Si	2	2	6	2	2					
15 P	2	2	6	2	3					
16 S	2	2	6	2	4					
17 Cl	2	2	6	2	5					
18 A	2	2	6	2	6					
19 K	2	2	6	2	6		1			
20 Ca	2	2	6	2	6		2			
21 Sc	2	2	6	2	6	1	2			
22 Ti	2	2	6	2	6	2	2			
23 V	2	2	6	2	6	3	2			
24 Cr	2	2	6	2	6	5	1			
25 Mn	2	2	6	2	6	5	2			
26 Fe	2	2	6	2	6	6	2			
27 Co	2	2	6	2	6	7	2			
28 Ni	2	2	6	2	6	8	2			
29 Cu	2	2	6	2	6	10	1			
30 Zn	2	2	6	2	6	10	2			
31 Ga	2	2	6	2	6	10	2	1		
32 Ge	2	2	6	2	6	10	2	2		
33 As	2	2	6	2	6	10	2	3		
34 Se	2	2	6	2	6	10	2	4		
35 Br	2	2	6	2	6	10	2	5		
36 Kr	2	2	6	2	6	10	2	6		

ATOMIC STRUCTURES (2)

<i>Element and Atomic Number.</i>	<i>Principal and Secondary Quantum Numbers.</i>										
	n= 1	2	3	4				5			
	l= —	—	—	0	1	2	3	0	1	2	0
37 Rb	2	8	18	2	6			1			
38 Sr	2	8	18	2	6			2			
39 Yt	2	8	18	2	6	1		2			
40 Zr	2	8	18	2	6	2		2			
41 Nb	2	8	18	2	6	4		1			
42 Mo	2	8	18	2	6	5		1			
43 Ma	2	8	18	2	6	6		1			
44 Ru	2	8	18	2	6	7		1			
45 Rh	2	8	18	2	6	8		1			
46 Pd	2	8	18	2	6	10		—			
47 Ag	2	8	18	2	6	10		1			
48 Cd	2	8	18	2	6	10		2			
49 In	2	8	18	2	6	10		2	1		
50 Sn	2	8	18	2	6	10		2	2		
51 Sb	2	8	18	2	6	10		2	3		
52 Te	2	8	18	2	6	10		2	4		
53 I	2	8	18	2	6	10		2	5		
54 Xe	2	8	18	2	6	10		2	6		
55 Cs	2	8	18	2	6	10		2	6		1
56 Ba	2	8	18	2	6	10		2	6		2
57 La	2	8	18	2	6	10		2	6	1	2
58 Ce	2	8	18	2	6	10	1	2	6	1	2
59 Pr	2	8	18	2	6	10	2	2	6	1	2
60 Nd	2	8	18	2	6	10	3	2	6	1	2
61 Il	2	8	18	2	6	10	4	2	6	1	2
62 Sm	2	8	18	2	6	10	5	2	6	1	2
63 Eu	2	8	18	2	6	10	6	2	6	1	2
64 Gd	2	8	18	2	6	10	7	2	6	1	2
65 Tb	2	8	18	2	6	10	8	2	6	1	2
66 Ds	2	8	18	2	6	10	9	2	6	1	2
67 Ho	2	8	18	2	6	10	10	2	6	1	2
68 Er	2	8	18	2	6	10	11	2	6	1	2
69 Tm	2	8	18	2	6	10	12	2	6	1	2
70 Yb	2	8	18	2	6	10	13	2	6	1	2
71 Lu	2	8	18	2	6	10	14	2	7	1	2
72 Hf	2	8	18	2	6	10	14	2	6	2	2

ATOMIC STRUCTURES (3)

<i>Element and Atomic Number.</i>	<i>Principal and Secondary Quantum Numbers.</i>										
	n = 1	2	3	4	5			6			7
	l = —				1	2	3	1	2	3	1
73 Ta		2	8	18	32	2	6	3	2		
74 W		2	8	18	32	2	6	4	2		
75 Re		2	8	18	32	2	6	5	2		
76 Os		2	8	18	32	2	6	6	2		
77 Ir		2	8	18	32	2	6	7	2		
78 Pt		2	8	18	32	2	6	8	2		
79 Au		2	8	18	32	2	6	10	1		
80 Hg		2	8	18	32	2	6	10	2		
81 Tl		2	8	18	32	2	6	10	2	1	
82 Pb		2	8	18	32	2	6	10	2	2	
83 Bi		2	8	18	32	2	6	10	2	3	
84 Po		2	8	18	32	2	6	10	2	4	
85 —		2	8	18	32	2	6	10	2	5	
86 Em		2	8	18	32	2	6	10	2	6	
87 —		2	8	18	32	2	6	10	2	6	1
88 Ra		2	8	18	32	2	6	10	2	6	2
89 Ac		2	8	18	32	2	6	10	2	6	1
90 Th		2	8	18	32	2	6	10	2	6	3
91 Pa		2	8	18	32	2	6	10	2	6	4
92 U		2	8	18	32	2	6	10	2	6	5

2. The Crystal Structures of the Metals

The crystal structures of the metallic elements are of interest from our point of view, because they show very clearly the conditions under which the metallic type of bond comes into being, and also because the inter-atomic distances are in some cases closely connected with the atomic structures, and so give an indication of the state of the atoms in the solid crystal. If we omit the elements to the extreme right of the Periodic Table, we find that, as regards their crystal structures, the elements fall into three main classes, which we have indicated by heavy lines in the redrawn diagram for the Periodic Classification shown in Fig. 63. Those elements lying in the left-hand class, which we have denoted Class I, crystallize in one of three typical metallic structures. These are the body-centred cubic structure in which each atom has eight equidistant neighbours, the face-centred

cube in which each atom has twelve equidistant neighbours, and the close-packed hexagonal structure, in which each atom has twelve equidistant neighbours if the axial ratio $\left(\frac{c}{a}\right)$ equals 1.63, whilst if the axial ratio is not exactly 1.63—for some metals it is 1.59—the twelve neighbours fall into two sets of six, at slightly different distances. So far as the evidence goes at present, these elements form typical metallic structures in which the interatomic distances follow the definite laws to which we shall refer

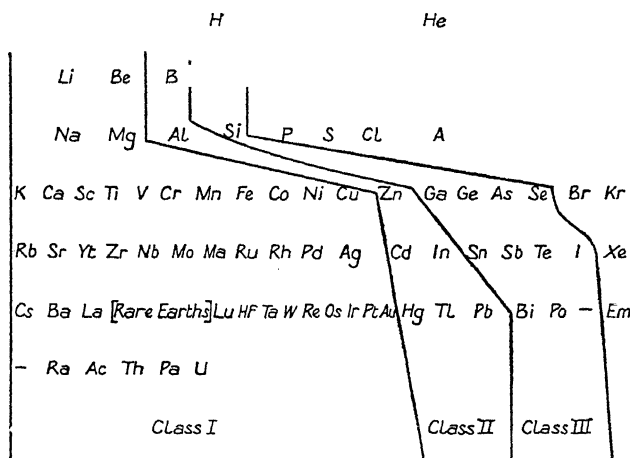


FIG. 63.

below. The only exception to this general rule is manganese, which crystallizes in complex structures.

The second class begins with aluminium, and includes zinc in the third period, cadmium and indium in the fourth, and mercury, thallium, and lead in the fifth period. Some of these elements have the normal *type* of metallic structure, but the interatomic distances do not follow the general rules, and indicate that the ionization is incomplete.

The third class, which includes many of the border line metals* such as arsenic, antimony, and bismuth, is characterized by forming crystal structures of such a type that each atom has

* For simplicity we have drawn the lines in Fig. 63 so as to include the Rare Earths, Masurium, Lutecium, Actinium, and Protoactium in Class I, Boron in Class II, and Polonium in Class III, but these structures have not yet been investigated.

$(8 - N)$ neighbours, where N is the number of the group to which the element belongs. In the case of iodine, for example, in Group VII, the structure is such that the atoms are arranged in pairs, so that each has one close neighbour, the remaining inter-atomic distances being considerably greater. In Group VI (selenium and tellurium) the space group is D_3^4 or D_3^6 , and the structure is of such a nature that the atoms are arranged in long spiral chains, so that each has two close neighbours. In Group V, arsenic, antimony, and bismuth crystallize in the rhombohedral hexagonal type, space group D_3^5d , in which the atoms are arranged in double layers so that each has three close neighbours. In Group IV, carbon (diamond), silicon, germanium, and grey tin crystallize in the diamond type of structure in which each atom has four neighbours, whilst in Group III, the single example, gallium, has, according to Jaegar, Terpstra, and Westenbrink,¹ a curious double layer structure, space Group $D_4^{16}h$, in which each atom is in close contact with one other in its own layer, and four others in the next layer, thus making five neighbours in all.

The most obvious explanation of this simple connexion between the crystal structure and the number of the group, is that just as in the co-valent compounds of chemistry, an atom of Group N completes its octet of electrons by sharing one electron with each of $(8 - N)$ other atoms, so, in the crystals of those elements obeying the $(8 - N)$ rule, the octet is completed by each atom taking $(8 - N)$ neighbours, and sharing one electron with each. This explanation was realized as long ago as 1924 by A. J. Bradley,² and has since been discussed in detail by Hume-Rothery,³ whilst J. D. Bernal⁴ has pointed out that the presence of co-valent bonds is indicated by the marked diamagnetism which is shown by crystals such as those of antimony. If this point of view be accepted, the abnormal 'metallic' properties of these borderline metals are at once accounted for, since it implies that each valency electron is associated with a particular pair of atoms, and so is no longer free. In the case of selenium and tellurium, for example, we are to look upon the atoms as bound into spiral chains by co-valent bonds, so that each chain is in effect an immense molecule, and the different chains are bound together by forces which may be of a molecular nature, and similar to those which hold the molecules together in the crystals of organic chemistry. Similarly in the case of arsenic, antimony, and bismuth, where every atom has three close neighbours, each double layer of atoms is to be considered as one huge molecule,

and the double layers are held together by molecular forces. On the other hand in Group IV, the co-valent linkages account for the entire structure, since the tetrahedral arrangement throughout space enables the whole crystal to be bound together.

The first objection to an explanation on these lines is that if the elements in Groups IV to VII, to which we have assigned co-valent and molecular structures, are really of this nature, they should be non-conductors, since all the valency electrons should be required for the co-valent bonds. The answer to this question clearly depends upon the stability of the co-valent bonds which confine each electron to two atoms. If these bonds are very stable, we shall expect the substance to be an insulator at all except the highest potential differences, and this condition clearly exists in the case of the diamond. On the other hand if the co-valent linkages are not so stable, we shall expect a limited conductivity to occur as the co-valent electrons are set free, and the effect of temperature upon resistance will be the result of two opposing tendencies. On the one hand, rise of temperature will liberate electrons, and so diminish the resistance, whilst, on the other hand, the increasing amplitude of the atomic vibrations with increase of temperature, will interfere with the passage of the electrons in the usual way. We shall therefore expect the resistance to have a negative temperature coefficient over the range of temperature for which the increase in the number of electrons outweighs the increasing amplitude of the atomic vibrations, and a positive temperature coefficient when the increase in the amplitude of the vibrations is predominant. We shall thus expect the phenomenon of minimum resistance, and, further, since, in accordance with general principles, the co-valent bond becomes less stable as we go down the Periodic Table, we shall expect the minimum point on the resistance curve to occur at lower temperatures in the later members of a group. In actual fact this is exactly what happens. In Group IV, for example, silicon has a negative temperature coefficient of resistance up to a high temperature where polymorphic transformations occur. Germanium shows a minimum resistance at -116°C. , whilst, in the case of grey tin, the temperature coefficient remains positive down to very low temperatures, although it has been concluded by Bidwell⁵ that the resistance curves here show a slight inflexion as though a minimum were being approached. In Group VI, tellurium shows a minimum resistance at the very low temperature of -225°C. , whilst selenium shows all the abnormalities

in connexion with the effect of light upon resistance, the failure of Ohm's Law, &c., which are clearly consistent with the view that the crystal contains co-valent linkages from which electrons are readily set free. It is only in Group V that the agreement is not so satisfactory, since although arsenic, antimony, and bismuth are all characterized by retaining an abnormally high resistance at very low temperatures, the resistance of arsenic reaches a constant value at temperatures as low as that of liquid helium, and the phenomenon of minimum resistance is not found. In this connexion it has been suggested by J. D. Bernal that in this group, where each atom has five valency electrons of which three are shared with neighbouring atoms so as to complete the octet, the remaining two unshared electrons whilst still mainly associated with the one atom, may yet be capable of interchange.

In general, however, the evidence from the crystal structure as to the co-valent and molecular nature of the crystals of the elements in Class III of Fig. 63 is in excellent agreement with their abnormal electrical properties, and we may in fact almost say that these elements are not really metals at all in the crystalline state, but are simple co-valent and molecular structures, in which the metallic properties only occur as the result of the 'decomposition' or breakdown of the co-valent bonds. In attempting to understand the nature of true metals, therefore, we should not pay too much attention to the properties of these abnormal elements, however interesting they may be in themselves. It is indeed one of the great misfortunes of the branch of science with which we have been dealing, that so much of the work, both practical and theoretical, should have been concentrated upon elements which are essentially abnormal.

When, however, we reach the elements in which there are less than four available valency electrons, it is clear that each atom can no longer complete an octet by sharing one electron with each of $(8-N)$ neighbours, because there are not enough electrons available. It is probable that it is here that we have the real underlying cause of the formation of the metallic bond. When there are not sufficient electrons available to enable the octet to be completed by each atom sharing one electron with each of its neighbours, the need arises for a new kind of bond in which an electron can serve for more than two atoms, and so the metallic linkage comes into being, and is apparently favoured by three structures, the body-centred cube, the face-centred cube, and the close packed hexagon, of which the last two are 'close

packed' structures, that is to say structures which can be obtained by the simple close packing of spheres, or of very slightly oblate spheroids if the axial ratio is not exactly 1.63 in the close packed hexagonal structure. From this point of view, therefore, the metallic linkage is to be looked upon as a kind of co-valent bond, in which an electron serves for several atoms, instead of being confined to two alone as in the simple co-valent structures.

It is here that the structure of gallium is so particularly interesting if the work of Jaegar, Terpstra, and Westenbrink be correct. For in spite of the fact that the full number of electrons necessary to form an octet by simple co-valent linkages is no longer available, the tendency to form the $(8-N)$ type of structure is still found, whilst at the same time the curious double layer arrangement is in some ways like a much distorted close packed structure. It seems, however, to be almost certain that most of the linkages are co-valent, for the metal shows marked diamagnetism, volume contraction, and fall in resistance on melting, just as with bismuth and antimony. But whether the remaining bonds are metallic or molecular is less certain, although the fact that the element is supra-conducting suggests a purely metallic bond unless a low temperature transformation occurs. Unfortunately, although the structure deduced by Jaegar, Terpstra, and Westenbrink may well be correct, the evidence is not as entirely conclusive⁶ as in the case of the other elements to which we have referred, and we shall not therefore discuss the matter further.

The next point to which we may refer is the connexion between the inter-atomic distance in the crystals of the elements, and the corresponding atomic structures, since this gives an indication of the state in which the atoms exist. On page 303 we have explained how the regular sequence in the Periodic Table of the elements is the result of the building up of the successive shells of electrons, and we have seen how the transitional elements, and those of the rare earth group, are the result of the fact that, in the electron shells of higher quantum number, groups of 8 or 18 electrons have a provisional stability, and later expand into completed groups of 18 and 32 electrons. If we are to understand the factors which affect the inter-atomic distances in the crystals of the elements, we have, therefore, to distinguish between those electrons which remain attached wholly to one atom, and those which are either 'free' or shared between two or more atoms. In a crystal of sodium for example, we have a nucleus with a charge

of $11e$, where e is the charge on one electron. This is surrounded by a shell of 2 electrons in 1 quantum orbits, and a second shell of 8 electrons in 2 quantum orbits, thus leaving one free electron to account for the metallic properties. In the free atom of sodium this remaining electron would be in a 3 quantum orbit, but in the crystal, owing to the mutual interaction of the ions, this is no longer necessarily the case, and if we accept the new theories, the energy of the free electrons is of course given by the Fermi-Dirac equations. In this case therefore it is the electrons in 2 quantum orbits which constitute the outermost shell of electrons in the ion or atomic core, and it is the quantum number of this group of electrons which appears to determine the 'size' of the atom, and the inter-atomic distance in the crystal. In the same way in the case of potassium, rubidium, and caesium, the outermost shells of electrons in the ion or atomic core are composed of electrons in 3, 4, and 5 quantum orbits respectively, and for convenience we shall denote by n the principal quantum number of this outermost shell of electrons in the ion or atomic core. These orbits will not, however, be the same as those for the corresponding quantum numbers of a hydrogen atom, for the charge on the nucleus (Ze) has to be taken into account, since an increase in Z diminishes the 'size' of an electron shell of given quantum number. The effect of increasing Z is, however, to some extent counterbalanced by the 'screening action' of the inner shells of electrons, but fortunately these mutual effects are apparently related in a comparatively simple way, so that the general principles underlying the interatomic distances can be seen. Considered qualitatively it is clear that the relation must be of such a type that Z exerts an effect to make the distance smaller, and that this effect will be continuous except in so far as it may be modified by the screening action. On the other hand n should appear as a discontinuous factor making the inter-atomic distance larger as the successive shells of electrons are built up. It has been shown by Hume-Rothery⁷ that this expectation is fulfilled in such a way that if d be the inter-atomic distance in the crystal of the element, Z the atomic number, and n the principal quantum number of the outermost group of electrons in the ion or atomic core, then in any one sub-group of the periodic table, the value of d is given by a relation of the type

$$\frac{d}{n} = \left(\frac{1}{aZ} \right)^x.$$

This relation, which has been called the Law of Sub-Groups, implies that if $\log \frac{d}{n}$ be plotted against $\log Z$ straight lines are formed by the elements in any one sub-group, and Figs. 64 and 65 show how well this is fulfilled.

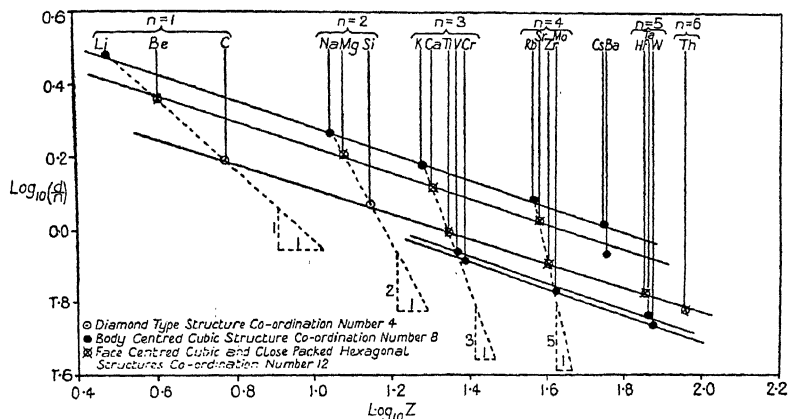


FIG. 64.

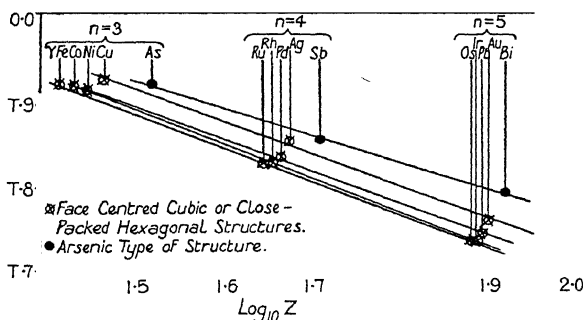


FIG. 65.

For the three groups, I A, II A, and IV A, immediately following the inert gases (Group III A cannot be tested owing to lack of data) the slopes of the lines in Fig. 64 are almost identical, and are nearly equal to $-\frac{1}{3}$, so that the relation is here very nearly $\frac{d^3}{n^3} = \frac{1}{aZ}$, but for the later groups the slope increases.

It was shown further that for the elements at the beginning of

the first *Period* the inter-atomic distance varies as $\frac{1}{Z}$, so that the dotted line in Fig. 64 has a slope of 45° . This relation together with that for the sub-groups enables us to fix the first three lines in Fig. 64 in terms of only two constants, since the slopes of the lines are practically the same, but the curious fact then emerges that the dotted lines connecting the elements at the beginning of the later *Periods* also have whole number gradients, so that at the beginning of the *Periods* the distances vary as $\frac{1}{Z}$, $\frac{1}{Z^2}$, $\frac{1}{Z^3}$, and $\frac{1}{Z^5}$. These relations are connected with the screening effects of the different shells of electrons, and the jump from $\frac{1}{Z^3}$ to $\frac{1}{Z^5}$ corresponds to the building up of the 18 group which takes place in the third period. The details of these relations have been discussed by Hume-Rothery,⁷ but these need not concern us here, since they involve secondary effects such as the co-ordination number,* and the number of electrons in the shell.† From our point of view, the first and most interesting fact is that there seems to be little difference between the metallic type of bond, and the purely co-valent bond found in structures such as that of the diamond. In the first *Period*, apart from a slight correction for the effect of co-ordination number, the inter-atomic distances in lithium, beryllium, and carbon vary simply as $\frac{1}{Z}$, and, if we

* *The Co-ordination Number* is the number of nearest neighbours which each atom possesses in the structure.

† A point which may, however, be mentioned for the sake of completeness is that in the close packed hexagonal structures where the axial ratio $\frac{c}{a}$ is not exactly that of close packed spheres, it is the distance of approach given by the value of a which is considered in the above relations. The justification for this is that in the case of cobalt, which crystallizes in both the face-centred cubic, and hexagonal close packed ($\frac{c}{a} = 1.59$) structures, it is the value of a which agrees with the inter-atomic distance in the face-centred cubic form. It must be admitted that this selection of the value of a as the quantity to be considered is slightly arbitrary, and its justification has been discussed in detail by Hume-Rothery.⁸ The metals for which the values of $\frac{c}{a}$ in the hexagonal close packed structure are not exactly 1.633 are Be, Mg, Ti, Zr, Hf, Ru, Os, and β Co, and in these the second distance of approach is from 0.5 per cent. to 2 per cent. less than the value of a which is used in the above figures.

consider the inter-atomic distances alone, there is nothing to suggest that we are passing from a metal to a non-metal. In the same way in passing down Group IV A, the points for carbon, silicon, titanium, zirconium, hafnium, and thorium lie on the same straight line, and there is nothing to suggest that metallic properties are appearing. This is of particular interest in view of the fact that titanium, in spite of having a normal close packed hexagonal structure shows the phenomenon of minimum electrical resistance at $+120^{\circ}$ C. As we have already explained, there is little difficulty in understanding the phenomenon of minimum resistance in the simple co-valent structures where the valency electrons are presumably shared between two atoms. But the fact that the same phenomenon is found in an element with the normal metallic structure, suggests that we have a continual transition from the purely co-valent bond found in the case of the diamond, through the intermediate type shown by titanium, to the purely metallic bond of the normal metals, and that this transition takes place without any marked effect upon the inter-atomic distances. From this point of view, therefore, we must, as in the theory of Bloch, look upon the crystal of a metal as one immense molecule, which differs only from a structure such as that of the diamond in the extent to which interchange between the different levels is possible.

The second point which is of interest for our purpose is that the inter-atomic distances in the crystals of the elements give an indication as to the state or degree of ionization in which the atoms exist. Unfortunately, except in the case of aluminium to which we shall refer later, the relations for Group III A cannot be tested, but the curves for the inter-atomic distances clearly suggest that the atoms in the crystals are uni-, di-, and tetra-valent in Groups I A, II A, and IV A respectively. For in the first two Periods it can hardly be doubted that in the elements carbon and silicon with the tetrahedral structures, the atoms are present in the normal 4-valent state, and the fact that in Fig. 64, the whole of the elements of Group IV A lie on a straight line parallel to those for the alkali and alkaline earth groups, clearly indicates that the elements of any one sub-group are in the same state. This is also confirmed by the fact that the dotted lines in Fig. 64 show that the inter-atomic distances decrease according to a regular law for the elements at the beginning of each Period, clearly suggesting that the degree of ionization is increasing regularly on passing from one element to the next.

On the other hand this regular decrease in the inter-atomic distances is not shown by the later members of the long Periods, and this of course is due to the transition process in the course of which the shells of 8 electrons, which have a provisional stability, are being converted into shells of 18. In order to see how the inter-atomic distances indicate the states of these atoms, we may now describe briefly some new empirical relations which have been found by Hume-Rothery.⁸ From Fig. 64 it will be appreciated that the inter-atomic distances vary as $\frac{1}{Z}$, $\frac{1}{Z^2}$, $\frac{1}{Z^3}$, and $\frac{1}{Z^5}$, for the elements at the beginning of the first four Periods respectively, and since the law of the sub-Groups $\frac{d}{n} = \left(\frac{1}{aZ}\right)^x$ involves the principal quantum number of the outermost shells of electrons of the atomic cores or ions, it is natural to inquire whether similar relations are shown by any other constants characteristic of the same electron groups. The quantities investigated by Hume-Rothery were the energy level terms $\frac{\nu}{R}^*$ which represent the work required to remove an electron from a particular shell, and to expel it from the atom. It has been shown by Hume-Rothery that the energy level terms and inter-atomic distances for the elements at the beginning of each Period, are related in such a way that if $\frac{\nu}{R}$ is the energy level term of the X_1 group of electrons in the outermost shell of the atomic core or ion, then wherever the inter-atomic distances vary as $\frac{1}{Z^x}$, there exists a linear relation between $\frac{\nu}{R}$ and Z^{2x} , and in many cases this linear relation becomes a simple proportionality between $\frac{\nu}{R}$ and Z^{2x} .

At the beginning of the first Period, for example, the inter-atomic distances vary as $\frac{1}{Z}$, and it is well known that a linear re-

* These energy level terms are obtained from the limiting frequencies of the X-ray series, and may be expressed in terms of $\frac{\nu}{R}$ where ν is the frequency, and R the Rydberg constant. The corresponding excitation potential in volts is equal to $13.54 \frac{\nu}{R}$.

lation exists between Z^2 and the $\frac{\nu}{R}$ energy level terms for the K , electrons.* In this case the straight line does not pass exactly through the origin, so that $\frac{\nu}{R}$ is not directly proportional to Z^2 , although a linear relation exists.

At the beginning of the second Period, the inter-atomic distances vary as $\frac{1}{Z^2}$, and examination has shown that in the elements from sodium to silicon, the $\frac{\nu}{R}$ values for the L_I electrons are almost exactly proportional to Z^4 , whilst for the L_{II} electrons $\frac{\nu}{R}$ is linear with regard to Z^4 although the straight line does not pass through the origin. For elements much later in the Periodic Table the $\frac{\nu}{R}$ values for both L_I and L_{II} electrons follow relations of the general type $\sqrt{\frac{\nu}{R}} = a(Z-s)$, but for the few elements following sodium, the linear relation between $\frac{\nu}{R}$ and Z^4 is surprisingly exact.

In the third Period the matter is complicated by the fact that the transition process begins in Group III A, so that whilst the free atoms of potassium and calcium have electronic structures (2)(8)(8)(1), and (2)(8)(8)(2) respectively, the structure of scandium is (2)(8)(9)(2), and *not* (2)(8)(8)(3). Here, however, examination shows that the $\frac{\nu}{R}$ values for the M_I electrons in potassium and calcium vary exactly as Z^6 ,† whilst, as we have already pointed out, the inter-atomic distances vary as $\frac{1}{Z^3}$ so that the general correspondence still persists at the beginning of the Period, although the variation of $\frac{\nu}{R}$ as Z^6 stops when the transition process in the free atoms begins at scandium, and as will be appreciated later the more detailed examination suggests

* The electrons in the shells of principal quantum numbers 1, 2, 3 . . . are often denoted as the K , L , M , . . . electrons.

† Since there are here two points only a linear relation is not established, but the exact variation as Z^6 for the two points can hardly be coincidence.

a method for determining the state of the atom in the solid crystal as compared with that in the free atom.

Finally in the fourth Period where the inter-atomic distances vary approximately as $\frac{1}{Z^5}$ —the actual slope of the line in the logarithmic diagram is -5.2 —the $\frac{\nu}{R}$ values for the N_I electrons vary almost as Z^{10} in rubidium and strontium, the exact slope of the line in the corresponding logarithmic diagram being 10.7 . Here as in the Third Period the variation as Z^{10} stops when the transition process begins in Group III. It can be seen therefore that for some reason, which is quite unknown, there is an almost complete correspondence between the relations for the inter-atomic distances and those for the $\frac{\nu}{R}$ values for the elements at the beginning of each Period. Where the inter-atomic distances vary as $\frac{1}{Z^x}$ at the beginning of a Period, the $\frac{\nu}{R}$ values vary as Z^{2x} for the X_I electrons of the outermost shell of the ion or atomic core.

We may now consider in greater detail the relations which have been traced for the elements of the third Period, and for this purpose reference should be made to Fig. 66, in the upper half of which $\text{Log } Z$ is plotted against $\text{Log } \frac{\nu}{R}$, where the $\frac{\nu}{R}$ terms are the energy values of the M_I electrons in the free atoms of the elements concerned. In order to appreciate this diagram it is necessary to consider how the transition process takes place and from the previous tables of atomic structures (p. 305) it will be seen that the numbers of electrons in the M shells (quantum number 3), and the N shells (quantum number 4) of the *free atoms* of these elements are as in the accompanying table. Potassium and calcium each have 8 electrons in the M shell, and as can be seen from Fig. 66, the slope of the $\frac{\nu}{R}$ line in the logarithmic diagram is $\frac{6}{1}$ indicating that the M_I energy level varies as Z^6 for these two elements.

From calcium to vanadium, successive steps result in the addition

Element.	M shell.	N shell.	
K	8	1	
Ca	8	2	
Sc	9	2	
Ti	10	2	
V	11	2	
Cr	13	1	
Mn	13	2	
Fe	14	2	
Co	15	2	
Ni	16	2	
Cu	18	1	

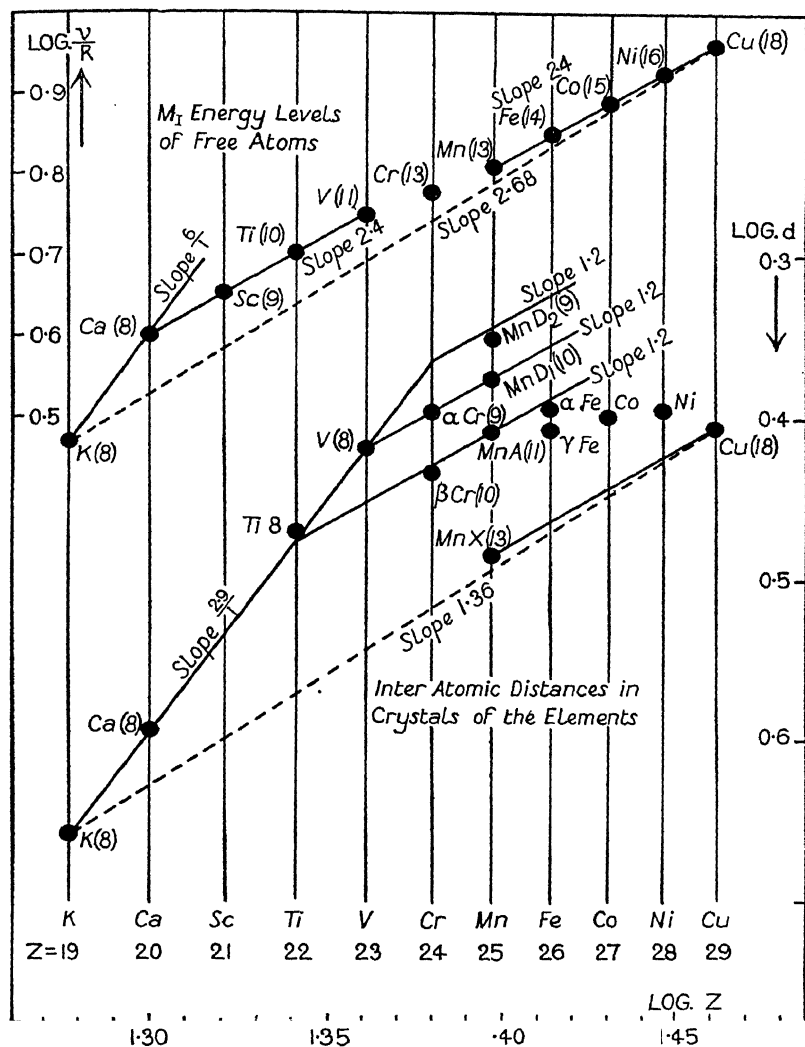


FIG. 66.

In the upper half of this figure $\text{Log } \frac{v}{R}$ is plotted against $\text{Log } Z$, and the scale for $\text{Log } \frac{v}{R}$ reads upwards. In the lower half of the figure $\text{Log } d$ is plotted against $\text{Log } Z$, the scale for $\text{Log } d$ being double that for $\text{Log } \frac{v}{R}$, and reading downwards. In this way, wherever lines are parallel in the two parts of the figure it implies that a variation of $\frac{v}{R}$ as $Z^{2.4}$ corresponds to a variation of d as $\frac{1}{Z^{2.4}}$.

of one electron, not to the valency group but to the M_3 subgroup of the M shell. During this stage it will be seen that $\log \frac{\nu}{R}$ increases linearly with $\log Z$, the slope of the line being 2.4. At chromium, however, this regular process stops, the structures of chromium and manganese being (2)(8)(13)(1), and (2)(8)(13)(2) respectively, and there is a corresponding break in the line. From manganese to nickel the transition process again proceeds regularly, each step resulting in the addition of one electron to the M shell, and over this range the points again lie on a line of slope of approximately 2.4. On the other hand if the available data are correct,* the point for copper lies almost exactly on this line in spite of the fact that there is a jump of two electrons in the M shell in passing from nickel ((2)(8)(16)(2)) to copper ((2)(8)(18)(1)).

In view of the correspondence, which we have described above, between the relations for the X_1 energy levels, and the interatomic distances, we have in the lower half of Fig. 66, plotted $\log d$ against $\log Z$, and as we have previously found that a variation of $\frac{\nu}{R}$ as Z^{2x} corresponds to a variation of d as $\frac{1}{Z^x}$, we have doubled the vertical scale for $\log d$, and have made this read downwards instead of upwards. In this way wherever lines are parallel in the two halves of the figure, it implies that the slope of the logarithmic line in the lower diagram is minus one-half that in the upper.

It will now be seen that the points for potassium, calcium, titanium, and vanadium lie on a straight line of slope almost exactly -3 (the actual slope of the best straight line is -2.9), as compared with the slope of $+6$ for the line through the points for potassium and calcium in the energy level diagram in the upper half of the figure. The conclusion which has been drawn here is that in the solid crystals of all these elements the M shell of 8 electrons remains unchanged throughout. We may note that this is in good agreement with the electrical conductivities per atom shown in Fig. 1 (p. 6), since these decrease regularly from potassium to titanium, but unfortunately data are not at present available for the conductivity of pure vanadium.

* The data used by Hume-Rothery were taken from the International Critical Tables and from a recent paper by Ray and Mukerjee (*Z. Phys.* 1929, 57, 352), and the details are discussed in Hume-Rothery's paper, to which reference should be made.

The next element, chromium, exists in two modifications, and the inter-atomic distances for each form are included in the diagram. It will be seen that the points for α chromium and vanadium lie on a straight line of gradient 1.2, or almost exactly minus one-half the gradient of the lines in the upper diagram which correspond to the addition of one electron per step to the M shell. In view of the general correspondence between the energy levels and inter-atomic distances, this clearly suggests that α chromium has nine electrons in the M shell, and we may therefore denote it Cr(9). It will now be seen that if we start from the point where the line through the points for potassium, calcium, titanium, &c., cuts the ordinate for titanium, and draw a line of gradient 1.2, this passes very nearly through the point for β chromium, and since it is two steps from titanium to chromium the conclusion suggested is that β chromium is Cr(10). The agreement here is not absolute, but the divergence is less than 1 per cent. The fact that the M shell of electrons has begun to expand at chromium is clearly in agreement with the electrical conductivities per atom in Fig. 1, which show a marked recovery at chromium, since we may naturally expect the free electrons to be less firmly bound as the number of the electrons in the M shell increases.

The next element, manganese, in its α modification has a very complex structure, the closest distance of approach being 2.24 \AA° , and when this point is included in Fig. 66, it lies just below that which would be indicated for Mn(9) by drawing a line of slope 1.2 through the intersection of the line through the points for potassium, calcium, &c., with the ordinate for chromium, but the difference is only just over 1 per cent. and may well be due to co-ordination effects, that is to say effects due to the fact that the atoms have not the same numbers of neighbours in the different structures. The actual structure of α manganese has been deduced by Bradley¹ and is very complicated, but it may be looked upon as a body-centred cubic structure in which each lattice point is replaced by a cluster of 29 atoms, which may be divided into four kinds which Bradley denotes X , A , D_1 , and D_2 atoms, of which the D_2 atoms occupy the smallest, and the X atoms the largest volume.

In view of the existence of these four types of atoms in the structure, it seemed natural to identify them with atoms in different states, and Hume-Rothery therefore extrapolated the above-mentioned lines of gradient 1.2 until they cut the ordinate

for manganese, and in this way tentatively predicted the values for Mn(10) and Mn(11) as 2.37 \AA° and 2.57 \AA° respectively. In view of the general correspondence between the inter-atomic distances and energy levels Hume-Rothery drew through the point for Cu(18) in the lower half of Fig. 66 a line parallel to that joining the points for Cu(18) and Mn(13), and in this way predicted the value for Mn(13) as 3.06 \AA° . The detailed examination of the various inter-atomic distances then showed that these were satisfactorily accounted for by the above figures, each of the predicted values finding its appropriate place in the complex structure assuming that the X atoms were Mn(13), the A atoms Mn(11), and the D_1 atoms Mn(10), whilst Bradley's value for the closest approach of the D_2 atoms, as we have explained above, is only slightly greater than that which the diagram would indicate for Mn(9).*

In addition to α manganese, there is a second modification β manganese, the complex structure of which has been investigated by Preston, and here the closest distance of approach is 2.365 \AA° , or almost the exact distance predicted above for Mn(10), whilst in the third modification, ' γ ' manganese, examined by Westgren, the closest distance of approach is 2.585 \AA° , which is very nearly equal to the value of 2.57 \AA° predicted for Mn(11), so that the general agreement of the inter-atomic distances in manganese is very striking.

When the inter-atomic distances in the two modifications of iron are inserted in the above diagram it will be seen that there is a distinct break in the regular process after Mn(11), and this apparently is the equivalent of the corresponding break which takes place in the energy level diagram after vanadium, which, in the free atom, also has eleven electrons in the M shell. It is clear that the break between (11) and (13) is one at which there is comparatively little difference between neighbouring states, and it is significant that in the inter-atomic distance diagram the metal iron, with its abnormal ferro-magnetic properties, comes just at this point. The existence of this break makes it unjustifiable to draw straight lines of gradient 1.2 in order to predict

* It should be noted that if the value for copper in the energy level diagram be incorrect, it is probable that the line in the lower half of Fig. 66 will give the value of Mn(14) and not Mn(13). The important point is that it is the line of gradient 1.2 through the point for copper which gives the required value for the Mn X atoms. This is discussed in the original.

values for atoms in states with more than eleven electrons in the M shell, so that the method breaks down beyond this point, although the marked increase in inter-atomic distance on passing from nickel to copper together with the general correspondence between the two parts of the diagram suggests that in the solid crystals the states of the atoms may be Fe(12 or 13), Co(18 or 14), Nickel(14 or 15), with a sudden increase in M shell on passing to Cu(18). Finally we may note that the dotted lines joining the points for potassium to copper are almost exactly parallel in the two halves of the diagram, the actual slopes being 1.86 and 2.68 ($= 2 \times 1.34$)

Space does not permit us to discuss these methods in further detail,* but in general it may be said that in so far as experimental evidence is available, these relations are completely confirmed in the fourth Period. Here the slope of the line through the points for rubidium and strontium in the logarithmic N_1 energy level diagram is 10.7, whilst in the corresponding inter-atomic distance diagram the points for rubidium, strontium, and zirconium lie on a line of slope -5.2 . In the energy level diagram the lines corresponding to the transition process have slopes of 2.68 when each step results in the addition of one electron to the N shell. The inter-atomic distance in niobium is not yet known, but the point for molybdenum lies exactly at the intersection of a line of slope 1.34 ($= \frac{1}{2} \times 2.68$) through the hypothetical point which the diagram would indicate for Nb(8), suggesting that molybdenum is Mo(9) and analogous to α chromium. Finally the lines joining the points for potassium and silver have gradients of $+4.4$ and -2.2 in the two halves of the figure, so that the general correspondence can hardly be a coincidence. In this case again the break in the transition process, which in the free atoms occurs between Zr(10) and Nb(12), prevents the straight lines from being extrapolated to the members of Group VIII.

* The reader who wishes to pursue this subject further must consult the original paper for several important details. The inter-atomic distances referred to are those at one-half the characteristic temperature. Further, as we have already explained (p. 314), in the close packed hexagonal structures for which the axial ratio c/a is not exactly the value (1.633) required for close packed spheres, the distance of approach considered in Fig. 66 is that given by the value of a . In cobalt and titanium, for example, there are distances of approach about 0.04 \AA less than those included in Fig. 66. These details affect the positions of the lines in Fig. 66 by amounts of the order 1 per cent., and are thus important when small differences are being dealt with, but for these points the original must be consulted.

In considering the value of such methods it must be admitted frankly that the meaning of these curious relations is at present quite unknown. Any simple explanation, as, for example, that the outermost shell of electrons in the atomic core or ion is directly responsible for the size of the atom, offers very great difficulties, particularly as the inter-atomic distances increase on passing from the inert gas argon to the next element, potassium. At present, therefore, the relations must be looked upon as a purely empirical correspondence between two series of constants, but the correspondence is so general that it can hardly be meaningless, and we have dealt with it here because it appears to offer some clue as to the state of the atoms in the metallic crystals. Unless the correspondence which has been traced is entirely fortuitous, the general process in the metals of the long Periods is now clear. In the free atoms the shells of 8 electrons begin to expand at Group III A, but in the solid crystals the same shell of 8 electrons persists as far as Group V. Then one or two electrons at a time are added to the group of 8 with a regular effect upon the inter-atomic distance, after which there is a sudden influx of electrons in order that the shell may contain 18 electrons at Group I A. These methods are admittedly a tentative groping in the dark for a means whereby the state of the atom may be obtained, but it is satisfactory to note that the conclusions are in good agreement with the electrical conductivities per atom so far as these have been determined. On the other hand, it must be recognized frankly that, until the meaning of these relations is more clear, the conclusions must not be looked upon as definitely proved, although the deductions made appear quite reasonable, since the correspondence is too general to be dismissed as a meaningless coincidence.

In the elements of the B sub-groups the inter-atomic distances are again most interesting. When we reach Group I B, the transition process is complete, and in the crystals of copper, silver, and gold, the outermost shell of electrons of the atomic core or ion contains a group of 18 electrons, which remains unaltered for the remainder of the Period. If therefore the normal process of ionization continues, we shall expect the inter-atomic distances to diminish as we pass along the Period, except in so far as this diminution may be masked or counter-balanced by the co-ordination numbers of the different crystal structures. Actually, however, the relations are by no means so simple. In the third Period, copper has the face-centred

cubic structure with inter-atomic distance 2.55 \AA , which is almost the same as that in gallium (2.56 \AA), and slightly greater than that in germanium (2.44 \AA). But in the case of zinc we find a close packed hexagonal structure with an axial ratio distinctly different from that for close packed spheres, and each atom has six neighbours at a distance 2.67 \AA , and six others at 2.92 \AA , both these distances *being greater than* the inter-atomic distance in copper. In the fourth period the relations are even more significant. Here the metal in Group I B, silver, has an inter-atomic distance of 2.88 \AA , and in Group IV B, grey tin, with the diamond type of structure, gives a somewhat smaller value, 2.80 \AA . There is, however, a second form of tin, white tin, in which the inter-atomic distances are very much greater, each atom having four neighbours at a distance of 3.07 \AA and two others at 3.16 \AA . The next metal, indium, in Group III possesses a very curious and interesting structure, which is face-centred tetragonal, but the axial ratio is only 1.06, so that it is only a very slightly distorted form of the face-centred cube. Each atom has four neighbours at a distance of 3.24 \AA and eight others at 3.33 \AA , both these distances being much greater than those in silver. Cadmium, like zinc, crystallizes in a close packed hexagonal structure with an axial ratio markedly different from that for close packed spheres, and the inter-atomic distances 2.96 \AA and 3.28 \AA are again greater than those in silver. In the fifth period, the same general process is carried a stage further. Here gold crystallizes in the face-centred cubic structure with an inter-atomic distance of 2.87 \AA , but there is no element later in the period with a smaller value than this. Thallium and lead have respectively hexagonal close packed and face-centred cubic structures, the inter-atomic distances being 3.40 \AA (Tl) and 3.48 \AA (Pb), both of which are markedly greater than the value for gold. The structure of solid mercury is simple rhombohedral,* but the closest distance of approach, 2.99 \AA , is again greater than that in gold.

The general significance of these relations is quite clear. We have already explained that the building up of a group of eight electrons takes place in steps of 2 and 6 electrons respectively, so that the outer electron groupings in atoms *in the free state* of the metals in Groups III B and IV B are (18)(2)(1) and (18)(2)(2) respectively, and the general facts of chemistry indi-

* This structure may be looked upon as a slightly distorted form of the face-centred cube.

cate clearly that the relative stability of the underlying $(18)(2)$ group increases as we go down the periods. Thus in Group III, the last member, thallium, has stable uni-valent $(18)(2)^+$ salts, and the tri-valent $(18)^{+++}$ salts are relatively unstable, but in the earlier members of the group it is the tri-valent salts which are the more stable. Taken in connexion with the evidence from the crystal structures, it may therefore be considered as almost certainly established that in indium, thallium, white tin, and lead, we have, in the metallic crystal, atomic cores with outer shells of $(18)(2)$ electrons, leaving one free electron in Group III and two in Group IV. On the other hand, in the diamond type co-valent structures of germanium and grey tin all of the valency electrons are used up to bind the atoms together, and this leaves atomic cores with the outer groups of (18) electrons, and the inter-atomic distances are therefore slightly less than those in the preceding uni-valent elements, copper, and silver, which have the same group of (18) electrons, but atomic numbers which are three units less than the following metals in Group IV. The fact that the structures for indium and white tin are not those of close packed spheres is probably the result of the fact that an incomplete group of two electrons, which has only just reached stability, is readily polarized, and so does not show perfect spherical symmetry in the crystal structure. It remains, however, to account for what may at first appear to be the rather arbitrary inclusion of aluminium with elements such as thallium and indium. The reason for this is that if the point for aluminium be inserted in Fig. 64, it appears to lie too high to fit in with the relations found for the neighbouring elements. A similar abnormality is found in the melting-points which in the first period increase steadily on passing from lithium to carbon, but which, in the second period, show a very small increase of only 8° on passing from magnesium (650°) to aluminium (658°), although there is the usual regular and marked increase on passing from sodium to magnesium, and magnesium to silicon. It seems probable therefore that aluminium, like indium and thallium, is only partly ionized in the solid crystal, and in this connexion it will be noticed that in Fig. 1 (p. 6) the conductivity per atom shows a slight increase, and not a decrease, in passing from magnesium to aluminium.

In the case of the Group II B elements, however, the position is not quite so clear, since here there are only two valency electrons per atom, and hence if the increase in the inter-atomic distance which takes place between Groups I B and II B be

ascribed to the formation of a sub-group of two electrons, there will be no free electrons left to account for the metallic properties. It has been suggested by Bernal that in zinc and cadmium, where the close packed hexagonal structures give each atom six neighbours in one plane, and three in each of the planes above and below, the structure is to be looked upon as a layer lattice in which the atoms in each plane or layer are bound together by 'homopolar' bonds, whilst the planes are held together by metallic bonds. The term 'homopolar' was used by Bernal for the bonds in structures such as grey tin and antimony, to which we have given the name co-valent, but it seems clear that in metals such as zinc and cadmium the bonds cannot be of a simple co-valent nature, because there are only two valency electrons per atom, so that if an electron be shared between two atoms, there are not sufficient electrons available to give each atom six neighbours and still to leave free electrons for the metallic linkages. A further difficulty in connexion with this point of view is that there seems to be no reason for the increase in inter-atomic distance in passing from Group I B to II B. An alternative explanation put forward by Hume-Rothery is that both zinc and cadmium are true metals but are only singly ionized in the solid crystal. Although at first this may seem rather improbable, this conception does in fact account for many of the facts. Thus in the A sub-groups the melting-points rise, and the inter-atomic distances diminish on passing from Group I to Group II, but in the B sub-groups the reverse is the case. In the same way the electrode potentials change in opposite directions, and the photo-electric threshold frequencies show a marked increase in passing from the alkalis to the alkaline earths, whilst there is no particular change in passing from Group I B to II B. These and other abnormalities are readily accounted for if zinc and cadmium are only singly ionized in the metallic crystal, the ions being larger than those in the preceding uni-valent metal, and, in the crystal structure, much less symmetrical. The structure of mercury is abnormal, but the inter-atomic distances are greater than those for gold, again suggesting that the metal is not fully ionized. It is for those reasons that the metals which we have placed in Class II in Fig. 63 are separated from those in Class I, but all these elements may be considered as true metals.

The crystal structures of the elements are thus of considerable interest from our point of view. They indicate clearly that the metallic bond comes into being at the exact stage at which there

are no longer sufficient valency electrons to enable the $(8-N)$ type of structure to be produced by purely co-valent bonds. The inter-atomic distances, and the relations connecting them with the quantum and atomic numbers, show that, as regards the distances, there is little difference between the metallic and the co-valent bond, and thus suggest that the metallic bond is of a co-valent nature, but differs from the normal co-valent bond in that the electron is no longer confined to two atoms alone. In the B sub-groups (and probably also for aluminium) the inter-atomic distances enable us to distinguish between those elements in which the ionization is complete, and those in which an incomplete group of one or two electrons is sufficiently definitely associated with one atom to produce a marked increase in the 'size' of the atom or the inter-atomic distance in the crystal; whilst in the A sub-groups the inter-atomic distances again give an indication of the state of the atoms in the solid, and we may note further that the conclusions formed in this way are in very good agreement with the atomic conductivities and their temperature variation for the different elements.

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3. The Composition and Nature of Secondary Solid Solutions and Intermetallic Compounds

In the introduction to this book we defined as intermetallic compounds those metallic phases of intermediate composition in which chemical combination, as exemplified by electron sharing or transference, had taken place, whilst by secondary solid solutions were implied phases of which the crystal structures differed from those of the parent elements, but in which the binding forces were in no wise different from those in ordinary metals. We may now discuss these points in somewhat greater detail, since some of the more recent evidence has thrown considerable light on the nature of these substances.

We may consider first those phases of fixed or very nearly fixed

composition in which there is general agreement that a definite compound is formed. Here we find that, except in a few compounds of the borderline metals such as Cu_3Sb , the most striking characteristic is that the ordinary rules of valency do not seem to be obeyed, but we have instead an apparently quite disconnected series of formulae. It was first pointed out by Hume-Rothery¹ that, when a truly metallic compound is formed, these irregular valency relations are quite to be expected. For it is the essence of chemical combination that the atoms share or exchange electrons in such a way that stable groupings are formed, and the so-called valency rules of the ordinary non-metallic compounds of chemistry are the result of two facts, namely, firstly, that certain definite numbers of electrons constitute stable groups (usually octets), and, secondly, that all the available valency electrons are used up, and bound into the stable groups. It is because all the valency electrons are employed, that the metallic properties of the constituent elements are lost in the compound. Consequently it is at once apparent that, if free electrons are left over so as to make a truly metallic compound, the valency relations must in general be different from those in the normal compounds in which all the valency electrons are used up. Little confidence can therefore be placed in the innumerable earlier attempts which were made to account for these abnormal valency relations by doubling or trebling the empirical formulae so as to obtain a very large molecule, in which, by a purely arbitrary arrangement, each atom could exert its normal valency. If the compound is really metallic, so that free electrons are present, we shall in general expect the ordinary valency rules to break down.

It was further suggested by Hume-Rothery that compounds which exhibited electrical conductivity should never be looked upon as normal valency compounds, even if their formulae, as in the examples Na_4Sn or Cu_3Sb , followed the ordinary valency rules. But this suggestion was undoubtedly over-exaggerated and incorrect. It is much more probable that just as there are crystal structures such as those of silicon and germanium, which are essentially co-valent structures but in which a limited electrical conductivity appears owing to the breakdown of the co-valent bonds, so there are compounds which are really normal valency compounds—either ionic or co-valent—but in which the metallic properties appear owing to the partial breakdown of the bonds. Such compounds might be expected to show the phenomenon of minimum resistance for the reasons which we

have already explained (see p. 309), but unfortunately little systematic examination of this kind appears to have been made.

The classification of these substances is indeed very difficult. In the first place the great majority of these compounds melt and vaporize at such high temperatures that it is often impossible to determine the true molecular weight from observations on the liquid or vapour, for even if the experimental difficulties can be overcome, the temperatures are usually sufficiently high to cause extensive decomposition. Consequently, in the great majority of cases, we only know the empirical formula, and cannot tell whether a compound is, for example, A_2B , A_4B_2 , A_6B_3 , &c. Apart from this, the majority of these compounds do not melt at constant temperature, so that a simple cast alloy contains several constituents, and prolonged annealing is necessary in order to obtain a specimen consisting of the homogeneous compound. If the compound does not melt below about 400°C ., it is usually possible to obtain a homogeneous specimen by annealing a fine-grained cast alloy for a sufficient time, but with alloys melting below 300° or 400°C . the reactions take place so slowly in the solid that even months of annealing may not ensure true equilibrium. In such cases the best course may be to prepare large single crystals by slowly cooling alloys of suitable composition under conditions in which the crystal can be removed above the temperature at which the later constituents would deposit if the whole alloy were allowed to become solid. There is, however, no doubt that a systematic examination of the electrical properties of intermetallic compounds at very low temperatures would greatly assist the classification of these substances, and that, in many cases, it should be possible to prepare suitable specimens. The value of such an examination would be greatly increased if accompanied by an x-ray investigation of the crystal structure, but in all such work the importance of suitable metallurgical treatment can hardly be over-estimated. In this connexion the physicist must recognize that it is useless to carry out experiments on specimens which are not in true equilibrium, or which are in a condition of strain or other physical abnormality, and he must realize further that the science of metallography has progressed sufficiently to indicate the correct treatment in the majority of cases. In all this work there is the greatest need for closer collaboration between the physicist and the metallurgist, and, as we shall now see, it is significant that it is in one of the few

cases where collaboration of this kind has been secured that results of interest have begun to accrue.

When we come to deal with the intermediate phases of variable composition which are met with in so many alloy systems, the position is naturally even more obscure, for whilst a properly determined equilibrium diagram gives the limits of composition of the phase concerned, it can only indicate the fundamental composition on which the solid solution is based in particularly favourable circumstances, as, for example, when the freezing-point curve rises to a maximum, such as that shown in Fig. 19 (p. 61) for the gold-zinc alloys. In other cases it is only when a systematic x-ray crystal analysis has been made that we can pick out any one composition in the solid solution as being fundamental. At present such studies are comparatively rare, and the position is complicated by the fact that sufficient care has not always been given to the heat treatment of the specimens used. Particularly interesting results have, however, been obtained in connexion with the structure of certain copper alloys, and the generalizations which have been made throw considerable light on the nature of intermediate alloy phases. The exact details of these crystal structures need not concern us here, but in a certain number of alloys of copper and silver it is found that phases of similar structure occur, and these same structures are sometimes found in gold alloys. If we start with pure copper, and then add increasing amounts of the second metal, the first phase is a simple solid solution of the second metal in copper, and has a face-centred cubic structure. In the general case, as the percentage of the second element is increased, these simple or ' α ' solid solutions reach their limit, and new phases are formed, which in several cases have a body-centred cubic structure, and are generally known as ' β ' phases. In some systems, such as the alloys of copper and zinc, the β phases are stable over a wide range of temperature, but more usually they are stable only at high temperatures and decompose on cooling. With increasing percentages of the second element, it is found that, in several cases, phases with the so-called ' γ ' structures are formed, whilst still later hexagonal close packed structures appear. The γ type of structure is complex, and is so called because it is the structure of the phase which had previously been known as ' γ ' brass. Of the phases corresponding to these different types of crystal structure, the α and β solid solutions have the properties of normal metals, but the phases with the ' γ ' and close packed structures

are hard and brittle, and for this reason have always been classed as compounds.

It was first pointed out by Hume-Rothery in 1926¹ that in some cases the compositions of the ' β ' phases were such that the ratio of valency electrons to atoms was approximately $3/2$. In the case of the copper-zinc alloys, for example, the ' β ' phase ranges about the equi-atomic composition CuZn, thus giving two atoms to three valency electrons (two from the di-valent zinc atom, and one from the copper atom). With copper-aluminium alloys, however, the β phase ranges round the composition Cu_3Al , giving four atoms to six valency electrons (one from each copper atom, and three from the tri-valent aluminium), so that the ratio $3/2$ is again maintained. Finally in the copper-tin system the corresponding phase is ranged round the composition Cu_3Sn , which again gives the ratio $3/2$, since there are now nine valency electrons (one from each copper atom, and four from the tetra-valent tin). In a more detailed study Westgren and Phragmen² have shown that phases with the characteristic ' β ' or body-centred cubic structure are found in the systems Ag-Mg, Ag-Zn, Ag-Cd, Au-Zn, Au-Cd, Cu-Al, Cu-Sn, and Cu-Zn, usually when the ratio of valency electrons to atoms is approximately $3/2$.

The same generalization was extended by Bradley and his collaborators,³ who showed that the very complex ' γ ' structures in the copper-zinc and copper-aluminium alloys are derived from the fundamental units Cu_5Zn_8 and Cu_9Al_4 , both of which correspond to the ratio 13 atoms to 21 valency electrons. In the copper-tin alloys the phase of corresponding structure has a very narrow range of composition which is definitely just not Cu_4Sn , but is almost exactly $\text{Cu}_{31}\text{Sn}_8$, which, in the most remarkable way, still gives the ratio $13/21$, since there are now $3 \times 13 = 39$ atoms, and $3 \times 21 = 63$ valency electrons. In this case, however, although the general γ type of structure is maintained, the exact distribution of the atoms is at present uncertain, since, according to Bernal,⁴ the unit cell contains 416 atoms which cannot be divided in exactly the ratio $31 : 8$. Westgren and Phragmen have concluded that phases with structures like that of γ brass occur in the systems Cu-Zn, Ag-Zn, Au-Zn, Ag-Cd, Ag-Hg, Cu-Cd, Cu-Al, and Cu-Sn when the ratio of the valency electrons to atoms is approximately $21/13$, but the most striking illustration of these regularities is probably shown by the work of Bradley and Gregory on the ternary alloys of copper,

zinc, and aluminium. These investigators find that, in the ternary alloys, the γ type of structure is retained so long as the ratio of valency electrons to atoms is 21:13. In other words, the atoms of copper, zinc, and aluminium may be interchanged, but as long as the ratio of valency electrons to atoms is kept at 21:13 the same γ type of crystal structure is found.

Finally it has been shown by Westgren and Phragmen that, in the systems Cu-Zn, Ag-Zn, Au-Zn, Ag-Cd, Au-Cd, Ag-Al, Au-Al, Ag-In, Cu-Sn, Ag-Sn, Cu-Sb, and Ag-Sb, the close packed hexagonal structure is most frequently found when the ratio of valency electrons to atoms is about 7:4.

In attempting to understand the significance of these most interesting relations, it must be emphasized that they are at present restricted to one particular series of alloys, those of copper, silver, and gold, and that there are most certainly exceptions to the general rules. It cannot be doubted that other factors, and particularly the atomic radii, influence the type of crystal structure, but on the whole it does not seem unreasonable to conclude that, when other conditions are favourable, the type of crystal structure in this series of alloys is determined principally by the ratio of atoms to valency electrons. In the case of the β phases these relations were interpreted by Hume-Rothery on the basis of the electron lattice theory, since they clearly suggested structures of positive ions and negative electrons with a fundamental ratio, and this could readily be understood in terms of interpenetrating lattices of atoms and electrons. Since these β phases have most of the properties of ordinary metals, with electrical conductivities rising to maxima at or near to the whole number ratios of atoms, it seems probable that they are simple secondary solid solutions in which the binding forces are of the same nature as those in pure metals. It has in fact been suggested by Rosenhain⁵ that the β phases may be looked upon as solid solutions in an allotropic form of copper, and in some ways this expresses the general idea very well. That is to say, just as a single metal, such as iron, may exist in different crystal structures at different temperatures, so alloys of two or more metals may form intermediate phases in which the crystal structures vary, but where the forces are in no way different from those in ordinary metals. But since the term solid solution in an allotropic form has generally been taken to imply a primary solid solution in the different allotropic forms of elements such as iron and chromium, in which the allotropes of the pure element

can be obtained, it appears better to avoid using the term in the case of alloys such as those of copper where the parent element exists in one form only, and for this reason the term secondary solid solution is to be preferred. The fact that the β phases so often occur when the ratio of valency electrons to atoms is 3:2 can then readily be explained on the basis of the electron lattice theory, whilst if we accept theories such as that of Bloch it implies that the whole crystal is to be looked upon as a gigantic molecule, in which the ratio of 3 electrons to 2 atoms enables a stable grouping to be formed, but in which free interchange of electrons is still possible.

In the case of the ' γ ' phases, however, the position is somewhat different. These substances are brittle, and in many ways quite distinct in properties from ordinary metals, and it has been shown by Bernal⁶ that they are very strongly diamagnetic, in marked contrast to their constituent elements. It was therefore suggested by Bernal that these substances were to be looked upon as co-valent or homopolar structures, in which the atoms were bound together by shared electrons in orbits which included more than one atom. That is to say, just as in the cases of silicon and germanium the whole crystal is to be looked upon as one immense molecule bound together by shared electrons (co-valent or homopolar bonds), so in the case of these γ phases the whole structure is one huge molecule, in which the atoms are bound together by homopolar bonds. This, of course, is in complete agreement with the maintenance of the ratio 13 atoms to 21 valency electrons, for as long as the structure requires a certain number of atoms to a certain number of co-valent bonds, it is immaterial as to which kind of atom provides the valency electrons. As pointed out by Bernal, the simplest example of this kind is that of the diamond type of structure, which is formed not only by the elements carbon, silicon, germanium, and grey tin with four valency electrons per atom, but also by a whole series of compounds such as GaAs, ZnSe, and CuBr, in which the only characteristic is that there are always eight valency electrons to two atoms. In the case of the γ phases, this explanation is confirmed in a most striking way by the solubility relations. For if these substances are really co-valent structures, in which there are so many homopolar bonds to so many atoms, we can at once see that there should be little or no solid solubility on the copper side of the composition corresponding to the ratio 13 atoms to 21 valency electrons. If, for example, we substitute a uni-valent

copper atom for a di-valent zinc atom in Cu_5Zn_8 , we reduce the number of valency electrons, and consequently, if the stability of the phase depends upon the presence of so many homopolar bonds, this substitution should not be possible. Actually it is found that, in contrast to the β phases, the γ phases show no solid solubility on the copper side of the compositions Cu_5Zn_8 , Cu_9Al_4 , and $\text{Cu}_{31}\text{Sn}_8$, so that these expectations are most strikingly confirmed. On the other hand there is not the same objection to having a slight excess of electrons above that required by the ratio 21/13, and consequently we find that these phases form a slight solution on the zinc, aluminium, or tin side. The range of the solid solution decreases from about 8 atomic per cent. in the case of the copper-zinc alloys to less than $\frac{1}{2}$ atomic per cent. in the copper-tin series, and this is, of course, to be expected, since the substitution of one atom of di-valent zinc for one atom of uni-valent copper adds only one more valency electron, whilst the substitution of an atom of tetra-valent tin adds no less than three.

If the above conceptions be true they should be reflected in the electrical conductivities of these substances, and examination now shows that this is most strikingly the case. We have already explained (p. 333 and also Chapter III) that in the case of the β phases the electrical conductivity rises to a maximum at or near the compositions CuZn , AuZn , &c., which correspond to the ratio 3 valency electrons to 2 atoms. But in the case of γ brass, the only one of the γ phases which appears to have been thoroughly examined, the exact reverse is the case, and, according to Puschin and Rjaschsky,⁷ the conductivity is a minimum at the copper-rich composition* Cu_5Zn_8 , and then increases with increasing zinc content. This is, of course, just what is to be expected if the ' γ ' phases are co-valent or homopolar structures. For if the structures are purely homopolar, then at the composition Cu_5Zn_8 all the valency electrons will be required to form the homopolar bonds, and free electrons will only be present in so far as the electrons are set free by the thermal oscillations, the presence of impurities, &c. But with an excess of electrons above the ratio 21/13, the presence of free electrons with an increase in conductivity is to be expected.† If the γ phases were purely homopolar,

* As we have explained above, there is little or no solid solubility on the copper-rich side of the composition Cu_5Zn_8 .

† Since this was written, Mr. J. D. Bernal has kindly told the author that he has found data for other ' γ ' phases, and that in each case the conductivity is a minimum at the composition corresponding to the ratio 21/13.

we should expect them to show the phenomenon of minimum resistance at a sufficiently low temperature, but it is of course possible that only some of the bonds are homopolar or co-valent, and that the normal metallic type of bond is also present. There is little doubt that a systematic examination of the electrical conductivities at low temperatures would be of the greatest value in helping to classify these most interesting alloy phases, but it is again almost impossible to over-estimate the importance of suitable heat treatment, and other precautions in the preparation of the specimens. At present it may be said that the evidence from the chemical compositions, crystal structures, and electrical conductivities is in substantial agreement. It suggests that, whilst both the β and γ structures tend to occur at constant ratios of atoms to valency electrons if conditions such as atomic volumes are favourable, the β phases are simple secondary solid solutions with the normal metallic type of binding, whilst the γ phases are co-valent or homopolar structures in which most, if not all of the electrons are shared between two or more atoms in co-valent linkages from which a few electrons may be set free by the thermal oscillations, the action of impurities, &c.

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4. The Problem of Supra-conductivity

The remarkable fact of supra-conductivity which we described previously (p. 11) has naturally aroused much interest and discussion, and at present opinion is divided as to whether supra-conductors constitute a special class of elements or not. We have already seen that, in the case of those elements which do not exhibit supra-conductivity, the resistance temperature curves, which are linear at high temperatures, eventually flatten, and become parallel to the temperature axis, so that a constant residual resistance is obtained. In the case of normal metals,*

* We are here omitting the co-valent structures found in elements such as germanium, antimony, &c.

this residual resistance becomes less as the amount of impurity in the metal diminishes, and it seems reasonable to conclude that in the great majority of the ordinary metallic elements, the resistance will vanish at the absolute zero. But this effect is quite distinct from the phenomenon of supra-conductivity, for the latter is a sudden vanishing of resistance at a temperature which may be as high as 7° Abs. (for lead). It is the suddenness of the phenomenon which is the real characteristic, and not the mere vanishing of the resistance, which can readily be understood in the light of the new theories. The second characteristic is that this sudden change in resistance is unaccompanied by any discontinuity in other properties, and we may note further that there is no correspondence between those metals which we usually describe as 'good conductors', and those which show supra-conductivity. The elements with the highest atomic conductivities are those in Groups I A and I B (the alkalis and the copper sub-group), and it is precisely these elements which have so far resisted all attempts to make them supra-conducting.

According to the point of view taken up by Kapitza¹ and others, all pure metals are to be looked upon as supra-conductors, but the supra-conductivity is obscured by the additional resistance due to impurities or strains, which for some reason does not vanish at low temperatures. Kapitza's conclusions were founded largely on the effects of a magnetic field upon resistance, since the resistance of a metal in the ordinary state is increased by a magnetic field, although the latter does not destroy supra-conductivity until the critical or threshold values of the field strength is reached. Kapitza therefore concluded that since the additional resistance produced by the magnetic field can vanish and leave the metal supra-conducting, so the residual resistance due to impurities, strains, &c., vanishes in the supra-conducting metals, but not in others.

This conception is, however, unsatisfactory in many ways. In the first place supra-conductivity has undoubtedly been observed in comparatively impure specimens of some metals, whilst others such as gold and silver have not shown the phenomenon in the highest obtainable degree of purity. Apart from this there seems to be absolutely no reason why the phenomenon should be restricted to some metals, which possess no special characteristics in other respects.

An alternative point of view has been put forward by Bartlett,² according to whom the residual resistance of the supra-conducting

metals disappears owing to the short-circuiting of the impure or imperfect patches by paths of the perfectly pure metal, for which the resistance suddenly becomes very much less than that of any normal metal. But there are many difficulties in this explanation, for again there seems to be no reason why the change should take place suddenly, or why the phenomenon should be confined to a comparatively few metals. Further, as pointed out by Kapitza, although in the case of lead, the resistance in the supra-conducting state has been shown to be less than 10^{-12} of that at 0°C ., in the majority of other metals the corresponding values have only been about 10^{-8} , and this is roughly of the same order as the ideal resistances of many metals at $1\text{--}2^{\circ}\text{Abs.}$, so that except for lead there is no experimental evidence that the supra-conductivity is of an entirely different order of magnitude. But the real difficulty is again the suddenness of the change, and for the present no satisfactory explanation has been found. It is perhaps significant that in the B Group elements, the metals for which supra-conductivity occurs at the highest temperatures are always those for which the crystal structures indicate that the ionization is incomplete, whilst in the elements of the A Groups those showing supra-conductivity (thorium and tantalum) again occupy positions in the Periodic Table in which the free atoms have energy levels which are very near together.

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5. The Problem of Conductivity

In reviewing the different theories which have been advanced in order to account for the electrical conductivity, and other properties of metals, it is important not to adopt the rival or partisan point of view. Each theory has been a genuine and sincere attempt to solve a most complex problem, and, in general, each has contributed something towards the solution. On the strictly quantitative side it must be admitted that all of the theories are unsatisfactory and incomplete. It may be taken as certain that the quantitative methods of the older theories, involving the treatment of the electrons as particles of a gas obeying the classical laws, are incorrect, although several of these theories gave a qualitative picture which contained a considerable element of truth. But the later theories are still in an elementary and

incomplete stage, for the mathematical difficulties have been so great that progress has only been made by assuming such a drastic simplification of the problem, that little more than the general order of magnitude can be expected. From some quarters there has in fact been a tendency to dismiss these new methods entirely, on the grounds that the simplifying assumptions were so crude as to make it a mere waste of time to erect a detailed mathematical theory. But this attitude is altogether too negative and unhelpful. For although the great need at the present time is for a wider and more systematic knowledge of the facts, it is only by investigating the problem in a simplified form, that it is possible to develop the mathematical technique necessary for the final solution.

But in spite of the present incomplete and transitional stage of the theory, certain general conclusions are gradually becoming established, some of which may concern properties other than those of a purely electrical nature. Of these the first is the recognition, as the result of both experiment and theory, that the conduction process takes place in such a way that the free paths of the electrons are large compared with the inter-atomic distances. This is indicated by the marked fall in conductivity of a pure metal when a solid solution is formed. A measurable increase in resistance can in fact be detected with amounts of impurity as small as one atom in 10^6 atoms of the pure metal, suggesting that the free path is of the order 10^2 times the inter-atomic distance. It seems, further, to be generally established that the conducting electrons exist in a metal in a condition such that their specific heat is negligible, but that at the same time their energy is large (see p. 296). Of the attempts to express this quantitatively, those involving the Fermi-Dirac statistics are by far the most successful, although at present the theories cannot claim to give more than the general order of magnitude. If the general type of argument used by Lennard-Jones (p. 295) be accepted, it seems highly probable that the distribution of electrons in a metal will in many ways resemble that of the lattice theories, although the lattice may well be of a dynamic rather than a static nature. If, therefore, any attempts are made to correlate properties such as cohesion with the theories which have been put forward from a consideration of the electrical characteristics, it seems probable that we must consider a metal as a vast molecule, in which the atoms are held together by attractions between the positive ions and the 'shared' valency electrons. This conclusion appears

inevitable, whether we adopt the dynamic lattice structure of Lennard-Jones, or the more indefinite theories of Bloch, and a preliminary investigation of this type has been made by Slater. The older crude ideas, which are so often found in metallurgical literature, involving directed attractions between the atoms, must thus be replaced by the conception of a metal as an array of mutually repulsive positive ions, held together by attractions towards the valency electrons.

Up to the present, comparatively little attention has been paid to the relative conductivities of the different elements, and this is largely due to the lack of reliable data over a range of temperature for metals in a state of high purity. The general periodic relations for the atomic conductivities shown in Fig. 1 (p. 6) are clear, and also the general way in which they are related to the state of ionization of the atoms. But there seems little doubt that a detailed comparison of the atomic conductivities of really pure metals should lead to results of great interest, whilst an investigation of the relative effects of different metals on the conductivities of alloy phases over a wide range of temperature should lead to results of value in connexion with the classification of such phases. At present comparisons of this kind are almost impossible owing to the lack of systematic and reliable data.

Even in the case of pure metals it is only in connexion with the electrical conductivity, the emission phenomena, and the specific heats that our knowledge of the facts is on a sufficiently firm foundation to justify the erection of any detailed quantitative theory. As explained in the Preface, we have not considered the specific heats, because these have already been dealt with in many other books. But even as regards the conductivity and emission phenomena, the reader can hardly fail to have been struck by the comparatively slight extent to which the facts have been systematized, and by the lack of reliable data for really pure metals in a condition of freedom from strain or other physical abnormality. It is indeed one of the great misfortunes in this branch of science that so much experimental work of the highest order should have been carried out on specimens which any scientific metallurgist would have condemned as unsuitable. In all this work there is thus the greatest need for closer collaboration between the physicist and the metallurgist, and such collaboration can only serve to benefit both branches of science. The Metallurgist must realize that although the problems with which the practical man is concerned may now seem to be far

removed from the electrical properties and theories which we have been describing, the latter will eventually include the whole of the characteristics of metals. He must recognize that it is only by the development of theories of this kind that Physical Metallurgy can be placed on a firm foundation, and removed from its present position in which it is little more than the study of apparently disconnected facts. On the other side, the Physicist must appreciate that the preparation of metallic specimens in a suitable condition for accurate work is in many ways a science in itself, and that the most elaborate physical measurements may lose all their value if the test pieces are not in a suitable state. He must realize that nearly all alloys require annealing or other heat treatment before they reach true equilibrium, and that, in many alloy systems, this treatment may require days or weeks before it is complete, whilst in the case of metallic elements the importance of purity and freedom from strain can hardly be over-estimated. In all these spheres the Physicist must recognize that, unless his measurements are made for technical purposes, he is only likely to add to the confusion if he carries out experiments on metals in an unsuitable condition. To some readers it may appear that this point is being over-elaborated, but the reference to the literature which has been made in the preparation of this book, has shown that the great majority of physical laboratories are still producing work which loses much of its value owing to the lack of comparatively simple precautions in the preparation of the specimens.

It is in connexion with the emission phenomena that the facts and the theory have been brought into the best agreement, but as will be appreciated from Chapter VII, it is just here that the knowledge of the facts is least convincing. For although the thermionic and strong field emission currents can be expressed satisfactorily by the equations of Richardson, Dushman, and Millikan, the predominance of the exponential term in these is so great, that, by suitable adjustment of the constants, the data may be expressed by a number of equations, whilst, apart from this, the constants are so much affected by secondary factors that critical comparison can hardly be made. There is therefore the greatest need for a systematic determination of the emission constants of the different metals in a state of high purity and freedom from strain, so that the relation between these constants, and the positions of the elements in the Periodic Table may be made more clear. In this connexion an examination of single crystals

should be of great value, for up to the present little attention has been paid to the effect of the grain boundaries upon the emission from ordinary poly-crystalline metal, although it is well known that the grain boundary material has, in many ways, properties which are quite distinct from those of the normal crystals.

But when we turn to the problems of conductivity and other electrical properties, we can only conclude that the position is far from satisfactory. If we look upon theory as a means whereby we may express our experimental data by equations of an accuracy comparable with that of the measurements, we can only admit that, except for purely empirical equations, or semi-empirical formulae such as those of Grüneisen, the theory is at present almost a complete failure. Alternatively, if we require our theory to enable us to classify the electrical constants of the different metals, so that we may trace their connexion with the Periodic Table and atomic structures, we can see that only the most elementary progress has yet been made, whilst in connexion with the study of alloys, apart from isolated investigations such as those of Norbury, we have little but a mass of disconnected facts.

From many points of view this position of the electronic theory of metals is only to be expected. For in all branches of Science, real progress is nearly always made in the same way. First the experimental facts are determined accurately and systematically. Secondly, the relations connecting these facts are discovered, and then, as the third step, the theory is erected, and tested by further experiment. The unsatisfactory position of the electronic theories of metals is largely the result of attempts having been made to erect detailed and complex mathematical theories, in order to explain facts for which accurate and systematic knowledge is almost entirely lacking. The need at the present time is not so much for further mathematical developments, but rather for a thorough and systematic determination of the electrical constants of metals, with special reference to their connexion with the Periodic Table and atomic structures. Such an investigation can only be secured by the closest collaboration between Physics and Metallurgy, and its results can only serve to benefit both Sciences.

For the present we may say that the problems in connexion with the electrical properties of metals remain essentially unsolved. But they are unsolved through lack of systematic and reliable experimental knowledge—not of theoretical speculation.

APPENDIX

The Theory of Bloch

§ 1.

IN Chapter V we have seen that the point of view adopted in the theory of Bloch¹ is that, while the conductivity electrons are free, their motion is not completely haphazard as in the 'gas' theories, but is rather a motion in a periodic field of force, of which the period is the same as that of the atomic lattice. The new mechanics then indicate that as long as the field of force is strictly periodic, the electrons are able to move unimpeded through the lattice of the atoms (or more properly ions), and that it is only when this strict periodicity is upset by the thermal oscillations that a resistance is created. In this method the mutual interaction of the electrons is ignored, and, in considering the motion of any one electron, the remaining electrons are assumed to be smoothed out or distributed with periodic density over the whole crystal, so that the particular electron considered moves in a periodic field. We have thus first to consider the motion of an electron in a strictly periodic field from the point of view of the new mechanics.

According to the Schrödinger theory the amplitude of probability $\psi(xyz)$ which corresponds to the energy E , and is independent of the time, conforms to the differential equation

$$\Delta\psi + \mu(E - V)\psi = 0 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where V is the electrostatic potential in which the electron moves in the lattice, and $\mu = \frac{8\pi^2m}{h^2}$.

We have next to consider how V will depend upon the co-ordinates (x, y, z) , and for this purpose we assume that the origin is at a lattice point, and that a, b, c , are the fundamental lattice vectors so that the vector of any point is given by

where g_1, g_2 , and g_3 are whole numbers. In this case V must satisfy the periodic conditions

$$V(r) = V(r + g_1a + g_2b + g_3c) \quad . \quad . \quad . \quad . \quad (2)$$

where g_1, g_2 , and g_3 are integers, and the vector r takes the place of x, y, z .

The characteristic values and proper solutions of equation (1) will then depend upon the boundary conditions to which they

must conform, and the most obvious assumption to make here is that ψ vanishes on the surface of the crystal, since the probability of finding an electron outside the crystal is negligible. This, however, lays too much stress upon the conditions at the surface, and introduces many difficulties in calculation, but these may be overcome by assuming, for the amplitude of probability of the electrons in the lattice, a cyclic condition similar to that introduced by Born and Karman for the elastic frequencies in their work on the specific heats of the crystal lattice. From this point of view, the properties are known for the whole lattice, however great, provided they are known in a sufficiently large parallelepiped which may be defined by vectors G_1a , G_2b , G_3c , where G_1 , G_2 , and G_3 are large integers. Once therefore we know a property for the fundamental portion G_1a , G_2b , G_3c , we can obtain it for the whole lattice by simple periodic repetition, and as we shall see later (page 355) this method of treating ψ waves similarly to elastic waves has great advantages when we deal with the problem of electrical resistance, where the two kinds of waves interact.

By using the theory of groups which was first introduced to problems in quantum mechanics by Wigner,² the conclusion is reached that every proper function can be expressed in the form

$$\sum_j e^{2\pi i \left(\frac{kx}{aG_1} + \frac{ly}{bG_2} + \frac{mz}{cG_3} \right)} \quad . \quad . \quad (3)$$

where k , l , m are whole numbers, and u_{klm} is a threefold periodic function with the periods a , b , and c , where $|a| = a$, $|b| = b$, and $|c| = c$. If we introduce the length of the vectors $aG_1 = K$, $bG_2 = L$, and $cG_3 = M$ which define the fundamental parallelepiped, this may be written in the form

$$\psi_{klm} = e^{2\pi i \left(\frac{kx}{K} + \frac{ly}{L} + \frac{mz}{M} \right)} u_{klm}(xyz). \quad . \quad . \quad . \quad (4)$$

The exact nature of the function u_{klm} remains undefined, since it depends not merely on the variation of the potential in the particular case, but also on other quantum numbers in addition to k , l , m . According to (4), therefore, the expression for the proper functions can be split up into a factor $e^{2\pi i \left(\frac{kx}{K} + \frac{ly}{L} + \frac{mz}{M} \right)}$, and a remainder depending only on the periodicity of the lattice, and this is equivalent to stating that we are concerned with plane de Broglie waves which are modulated in the rhythm of the lattice structure. It is this similarity of the proper function to that of the motion of an electron in the absence of forces, which gives the electrons in the lattice the mobility which is essential

for conductivity. According to Schrödinger,³ the current in the x direction corresponding to an electron in the state (k, l, m) is given by

$$s_{klm}^x = \frac{e\hbar}{4\pi im} \int \left(\bar{\psi}_{klm} \frac{\partial \psi_{klm}}{\partial x} - \psi_{klm} \frac{\partial \bar{\psi}_{klm}}{\partial x} \right) d\tau, \quad (5)$$

where the integration is to be carried out over the whole parallelepiped, and the proper functions (4) are to be orthogonal and normalized. This expression may be written in an alternative form, since, according to (1)

$$\bar{\psi} \Delta \psi - \psi \Delta \bar{\psi} = 0;$$

so that if we use Green's theorem

$$\begin{aligned} & \int x (\bar{\psi} \Delta \psi - \psi \Delta \bar{\psi}) d\tau + \int x [(\text{grad } \psi, \text{grad } \bar{\psi}) - (\text{grad } \bar{\psi}, \text{grad } \psi)] d\tau \\ &= - \int \left(\bar{\psi} \frac{\partial \psi}{\partial x} - \psi \frac{\partial \bar{\psi}}{\partial x} \right) d\tau + \int x \left(\bar{\psi} \frac{\partial \psi}{\partial n} - \psi \frac{\partial \bar{\psi}}{\partial n} \right) df = 0, \end{aligned}$$

where the last integral is taken over the whole surface of the fundamental parallelepiped, and $\frac{\partial}{\partial n}$ means differentiation along the normal. On account of the periodicity, the expressions $\bar{\psi} \frac{\partial \psi}{\partial n}$ and $\psi \frac{\partial \bar{\psi}}{\partial n}$ are equal and of opposite sign at corresponding points on the surface, so that a contribution is only made by the x faces, and we are left with

$$\begin{aligned} s_{klm}^x &= \frac{e\hbar}{4\pi im} \int \left(\bar{\psi}_{klm} \frac{\partial \psi_{klm}}{\partial x} - \psi_{klm} \frac{\partial \bar{\psi}_{klm}}{\partial x} \right) d\tau \\ &= K \frac{e\hbar}{4\pi im} \int \left(\bar{\psi}_{klm} \frac{\partial \psi_{klm}}{\partial x} - \psi_{klm} \frac{\partial \bar{\psi}_{klm}}{\partial x} \right) df, \quad (6) \end{aligned}$$

where the integral covers only the right-hand face. The proportionality with K is only apparent since the normalization of the ψ_{klm} must be taken into account, but since (6) is in general not zero, the state k, l, m corresponds to a definite momentum or velocity in the x direction, and we may now examine the effect of this from the two extreme cases of entirely free, and very tightly-bound electrons.

(a) *The case of Free Electrons.*

Here on account of the normalization we obtain from (4)

$$\psi_{klm} = \frac{1}{\sqrt{KLM}} e^{2\pi i \left(\frac{kx}{K} + \frac{ly}{L} + \frac{mz}{M} \right)},$$

so that in this extreme case the quasi-plane de Broglie waves actually become the known plane waves, and (6) becomes

$$s_{klm}^x = \frac{e}{m} \frac{kh}{K}, \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where $\frac{kh}{K}$ gives the momentum corresponding to the wave length $\frac{K}{k}$.

(b) *The Case of Very Strongly Bound Electrons.*

This case is very much more complex, but it may be considered as characterized by a potential V which is strongly negative in the immediate vicinity of each lattice point, but which rises sharply at distances of about half the lattice constant. At these places the proper functions and their first derivatives become very small, as has been shown by Hund.⁴ To see how the conductivity depends upon how tightly the electrons are bound, we have only to place the right-hand face of the fundamental parallelepiped in (6) midway between two lattice planes. The lattice planes are then only in places of high potential and so the expressions ψ and $\frac{\partial \psi}{\partial x}$ become very small, and vanish in the case of ideal insulators where the electrons are infinitely tightly bound. A more accurate picture can be obtained by considering equation (1) as a disturbance problem as was done by Heitler and London for the case of two hydrogen atoms, and since we are ignoring the interaction of the electrons, we may treat the question as a one body problem.

We may first express the potential of (1) as the sum of those due to the different lattice points, and strictly speaking we should include not merely the field due to the metal ion, but also that resulting from the presence of all the other conducting electrons. But this last effect is relatively small in the immediate vicinity of an atom, so that we may reasonably put simply the potentials of the ions. If the ion lies at the point

$$r_{g_1 g_2 g_3} = g_1 a + g_2 b + g_3 c$$

its potential is given by

$$U_{g_1 g_2 g_3}(xyz) = U(x - g_1 a, y - g_2 b, z - g_3 c)$$

and

$$V(xyz) = \sum_{g_1 g_2 g_3 = -\infty}^{+\infty} U_{g_1 g_2 g_3}(xyz) \quad . \quad . \quad . \quad (8)$$

If we now take the differential equation

$$\Delta \varphi_{g_1 g_2 g_3} + \mu(E - U_{g_1 g_2 g_3}) \varphi_{g_1 g_2 g_3} = 0 \quad . \quad . \quad (9)$$

which corresponds to the motion of an electron round one ion of the lattice considered as isolated, we may place that one of its real proper solutions (vanishing at infinity) which corresponds to the lowest proper value E_0 , as

$$\varphi_{g_1 g_2 g_3}(xyz) = \varphi(x - g_1 a, y - g_2 b, z - g_3 c). \quad . \quad . \quad (10)$$

If we neglect the action of the metal ions on their neighbours the degree of degeneracy is equal to the number of ions in the lattice, since each has the same energy E_0 . For the solution of (1) we may therefore assume that

$$E = E_0 + \epsilon, \quad \psi = \sum_{g_1 g_2 g_3} a_{g_1 g_2 g_3} \varphi_{g_1 g_2 g_3} + v. \quad . \quad . \quad (11)$$

where ϵ and v are small, so that we can neglect their products and higher powers. Then from (1) and (9) we obtain

$$\Delta v + \mu(E_0 - V)v = -\mu \sum_{g_1 g_2 g_3} a_{g_1 g_2 g_3} \varphi_{g_1 g_2 g_3} (\epsilon - V + U_{g_1 g_2 g_3}) \quad (12)$$

For the potential $U(xyz)$ surrounding an isolated ion, we assume that U becomes infinitely negative at the point $x = y = z = 0$, and that it vanishes at infinity and is already very small at a distance from the origin equal to about half the lattice spacing—this is justified by the use of (9). Then the proper functions $\varphi_{g_1 g_2 g_3}$ are almost zero except in the immediate vicinity of the point $(g_1 g_2 g_3)$, and if we consider them as normalized, and omit terms of the order v , we have

$$\int \varphi_{g_1 g_2 g_3} \varphi_{h_1 h_2 h_3} d\tau = \begin{cases} 1 & \text{when } g_1 = h_1, g_2 = h_2, g_3 = h_3, \\ 0 & \text{in all other cases.} \end{cases} \quad (13)$$

We assume further that the lattice is simple cubic, and that the functions $U(xyz)$ and $\varphi(xyz)$ are spherically symmetrical. In this case we may put

$$\int U'_{g_1 g_2 g_3} \varphi_{g_1 g_2 g_3} \varphi_{h_1 h_2 h_3} d\tau = \begin{cases} \alpha & \text{if } (h_1 h_2 h_3) = (g_1 g_2 g_3) \\ \beta & \text{if } (h_1 h_2 h_3) \text{ is near to } (g_1 g_2 g_3) \\ 0 & \text{in all other cases.} \end{cases}$$

Here α is the addition to E caused by the influence of neighbouring atoms, and β arises from the possibility of the interchange of electrons of neighbouring atoms, whilst $U' = V - U_{g_1 g_2 g_3}$.

To determine the unknown $a_{g_1 g_2 g_3}$ it can be shown that every function which is periodic in the fundamental parallelepiped is multiplied by a root of unity (i.e. a number say α such that $\alpha^G = 1$, where G is some whole number depending on the struc-

ture of the crystal) in moving from one lattice point to the next, so that neglecting the small additional factors we may put

$$\alpha_{g_1 g_2 g_3}^{klm} = e^{2\pi i \left(\frac{k g_1}{G_1} + \frac{l g_2}{G_2} + \frac{m g_3}{G_3} \right)}, \quad . \quad . \quad . \quad (14)$$

where k, l, m are whole numbers (see p. 344), and this satisfies the system of equations if

$$\epsilon_{klm} = \alpha - 2\beta \left(\cos \frac{2\pi k}{G_1} + \cos \frac{2\pi l}{G_2} + \cos \frac{2\pi m}{G_3} \right) . \quad (15)$$

so that the proper functions to zero approximation become

$$\psi_{klm} = \sum_{g_1 g_2 g_3 = -\infty}^{+\infty} e^{2\pi i \left(\frac{k g_1}{G_1} + \frac{l g_2}{G_2} + \frac{m g_3}{G_3} \right)} \varphi_{g_1 g_2 g_3} \quad . \quad . \quad . \quad (16)$$

and the corresponding disturbances of the proper values are obtained by giving the numbers k, l, m in (15) and (16) values from 1 to $G_1 G_2 G_3$. The original degree of degeneration of the electron states possible in the fundamental parallelepiped is thus reduced to the $G_1 G_2 G_3$ -th part.

By combining (16) with (6), the current corresponding to the state klm becomes

$$\begin{aligned} s_{klm}^x = K \frac{e}{m} \cdot \frac{\hbar}{2\pi} \sum_{\substack{g_1 g_2 g_3 \\ h_1 h_2 h_3}} \sin 2\pi \left[\frac{k}{G_1} (h_1 - g_1) + \frac{l}{G_2} (h_2 - g_2) \right. \\ \left. + \frac{m}{G_3} (h_3 - g_3) \right] \cdot \int \varphi_{g_1 g_2 g_3} \frac{\partial \varphi_{h_1 h_2 h_3}}{\partial x} df. \quad . \quad . \quad . \quad (17) \end{aligned}$$

The integration here covers the right-hand side of the parallelepiped between two lattice planes, and it differs from zero only if the lattice points $(g_1 g_2 g_3)$ and $(h_1 h_2 h_3)$ are either coincident or are neighbours separated by the right-hand surface. If the surface of integration separates the atoms $(g_1 g_2 g_3)$ and $(g_1 + 1, g_2, g_3)$ we have from reasons of symmetry

$$\left. \begin{aligned} \int \varphi_{g_1 g_2 g_3} \frac{\partial \varphi_{g_1+1, g_2 g_3}}{\partial x} df &= \int \varphi_{g_1+1, g_2 g_3} \frac{\partial \varphi_{g_1, g_2 g_3}}{\partial x} df = \Phi^x, \\ \int \varphi_{g_1 g_2 g_3} \frac{\partial \varphi_{g_1 g_2, g_3}}{\partial x} df &= \int \varphi_{g_1+1, g_2 g_3} \frac{\partial \varphi_{g_1 g_2 g_3}}{\partial x} df = -\Phi^x. \end{aligned} \right\} \quad (18)$$

Hence, since the number of lattice point pairs separated by the right-hand face is equal to $G_2 G_3$, and since $K = a G_1$, (17) may be written in the form

$$s_{klm}^x = a G_1 G_2 G_3 \cdot \frac{e \hbar \Phi^x}{\pi m} \sin \frac{2\pi k}{G_1}, \quad . \quad . \quad . \quad (19)$$

and by normalization the current in the x direction due to a single electron in the state klm is

$$s_{klm}^x = e \frac{a\hbar\Phi^x}{\pi m} \sin \frac{2\pi k}{G_1} \dots \dots \dots (20)$$

Equation (20) for the bound electrons thus corresponds to (7) for the case of completely free electrons.

§ 2. The Specific Heat of Bound Electrons

In the simple electron gas theory of Sommerfeld, the specific heat of the free electrons increases linearly with the temperature as long as $T \ll 10^4$ at which temperatures the gas is degenerate. In the case of the bound electrons, however, the position is different owing to the use of formulae (11) and (15). From these equations the energy corresponding to the state k, l, m is given by

$$E_{klm} = E_0 + \alpha - 2\beta \left(\cos \frac{2\pi k}{G_1} + \cos \frac{2\pi l}{G_2} + \cos \frac{2\pi m}{G_3} \right). \quad (21)$$

We may now assume the fundamental parallelepiped to be cubic, and to contain exactly one gram-molecule of the metal so that

$$G_1 = G_2 = G_3 = G, \text{ and } G^3 = L = \text{Loschmidt's number.}$$

Then G is of the order 10^8 , and we may assume that the expressions ξ, η, ζ defined by

$$\xi = \frac{2\pi k}{G}, \quad \eta = \frac{2\pi l}{G}, \quad \zeta = \frac{2\pi m}{G}$$

are continuously variable from $-\pi$ to $+\pi$, since the larger the fundamental parallelepiped, the closer together the stationary states, so that the distribution function $f(\xi\eta\zeta)$ which would be markedly discontinuous for a small unit, becomes a continuous function for a large one. This function gives the number of electrons in the element defined by

$$dk dl dm = \frac{L}{8\pi^3} d\xi d\eta d\zeta$$

and according to the Fermi-Dirac statistics is given by

$$f(\xi\eta\zeta) d\xi d\eta d\zeta = \frac{L}{8\pi^3} \frac{1}{A} \frac{d\xi d\eta d\zeta}{e^{\frac{2\beta}{kT} (\cos \xi + \cos \eta + \cos \zeta)} + 1} \dots \dots (22)$$

where the constant A can be determined because the number of electrons in the fundamental parallelepiped is known.

In the preceding section we have assumed that the original proper value of E_0 is single so that, even if the interaction be

considered, only one state defined by k, l, m corresponds to a definite value E_{klm} of the energy. In general, however, even if we neglect the spin, the original term E_0 will be degenerated, say λ times. If we assume that owing to the interaction, the energy of each of the λ states belonging to E_0 is split up in the same way, and that, owing to the spin, there may be two electrons in the same state, then if $n = \frac{N}{L}$ is the number of conducting electrons per atom, A is given by

$$\frac{N}{2\lambda L} = \frac{n}{2\lambda} = \kappa = \frac{1}{8\pi^3} \int \int \int_{-\pi}^{+\pi} \frac{d\xi d\eta d\zeta}{\frac{1}{A} e^{\frac{2\beta}{kT}(\cos\xi + \cos\eta + \cos\zeta)} + 1}. \quad (23)$$

and the total energy E is given by

$$E = N(E_0 + \alpha) - \frac{4\lambda L\beta}{8\pi^3} \int \int \int_{-\pi}^{+\pi} \frac{\cos\xi + \cos\eta + \cos\zeta}{\frac{1}{A} e^{\frac{2\beta}{kT}(\cos\xi + \cos\eta + \cos\zeta)} + 1} d\xi d\eta d\zeta \quad (24)$$

and the specific heat is given by $\frac{dE}{dT}$. For abbreviation we may write $\gamma = \frac{2\beta}{kT}$, and may consider the solutions for the two extreme cases $\gamma \ll 1$, and $\gamma \gg 1$.

1. $\gamma \ll 1$, or $T \gg \frac{2\beta}{k}$.

In this case the solution reduces to

$$E - N(E_0 + \alpha) = -\frac{6\lambda L\beta A}{(A+1)^2} \gamma = -3\kappa(1-\kappa)\lambda L \frac{(2\beta)^2}{kT},$$

and for the specific heat (per molecule) we obtain

$$C_v^e = \frac{\partial E}{\partial T} = 3\kappa(1-\kappa)\lambda L \cdot \frac{(2\beta)^2}{kT^2} = 3\kappa(1-\kappa)R\gamma^2, \quad (25)$$

where R is the gas-constant. The specific heat of the electron gas in a periodic field therefore varies as $\frac{1}{T^2}$ as long as the temperature is considerably above $T_0 = 2\beta/k$. The value of T_0 or of β depends on the height of the potential ridge between two atoms, and the lower this ridge, the more nearly are the electrons free and the greater is T_0 , and in the case of completely free electrons T_0 is of the order 10^4 which is the same temperature as that at which the simple electron gas of Sommerfeld changed from the degenerate

to the undegenerate state, though here our formula (21) is no longer valid quantitatively. In the case of tightly bound electrons, however, T_0 may be very much less.

2. $\gamma \gg 1$, or $T \ll \frac{2\beta}{k}$.

This case corresponds to the degenerate gas, and differs only from that of the 'gas' of Sommerfeld in the different way in which the energy E_{klm} depends on the quantum numbers. The solution obtained here involves simplifying approximations and is

$$E = N(E_0 + \alpha - 6\beta) + 2c\beta \frac{\lambda L}{5\pi^2} \varrho_0^5 \left[1 + \frac{5\pi^2}{12} \left(\frac{1}{c\gamma} \right)^2 \frac{1}{\varrho_0^4} \right]$$

where $c = \frac{\sin \varrho_0}{2\varrho_0}$, and $\varrho_0 = \sqrt[3]{6\pi^2 \kappa}$ is the critical velocity on the distribution curve. The resulting expression for the specific heat is

$$C_v^2 = \frac{\partial E}{\partial T} = \frac{\lambda L}{6} \frac{k^2}{2c\beta} \varrho_0 T = \frac{\lambda \varrho_0}{6c} R \cdot \frac{1}{\gamma}. \quad (26)$$

These expressions therefore require the specific heat of the firmly bound electrons, at very low temperatures, to increase in direct proportion to T , and to reach a maximum in the region $T \sim T_0$, and then to diminish as $\frac{1}{T^2}$. In actual practice a variation

of this general qualitative type has been found by Simon⁵ for grey tin and silicon, in which, as we have already seen (page 308), the crystal structure indicates that we have to do with a firmer kind of binding than in normal metals. With grey tin, on cooling, the specific heat varies as $\frac{1}{T^2}$ at high temperatures, reaches a maximum at 29°, but then diminishes exponentially instead of linearly as would be required by equation (26). The observations of Simon were in good agreement with a formula of Schottky⁶ which required the exponential type of variation at low temperatures, but deviations from this formula were found in the case of silicon so that the position is rather obscure, although the type of variation required by equation (26) is in general qualitative agreement with the specific heats of these particular metals.

§ 3. The Acceleration of the Electrons in a Homogeneous Electric Field

To investigate the electrical conductivity of a metallic crystal we have to consider firstly the way in which the motion of the electrons changes when a potential difference is applied, and

secondly how the electrons interact with the vibrations of the crystal lattice. In this line of approach we neglect the mutual interaction of the electrons, because the electrical conductivity is concerned only with the total momentum of the electron gas, which remains unaffected by interchange between the electrons, although it is influenced by the applied potential and the atomic vibrations. The first suggestion here is to start from a definite sharply-defined state, and to investigate how this may undergo transitions into other states owing to the action of the field. But in this case the uncertainty of position of the electrons would extend over the whole crystal, and we should have to consider places where the potential of the field had exceeded all limits. To avoid this difficulty we may build up a packet of waves which nearly vanishes at the edge of the fundamental parallelepiped but is large enough to require only proper functions belonging to a group of neighbouring states.

We assume, therefore, that at the time $t = 0$, we have a wave packet built up similarly to those used by Heisenberg⁷ and Kennard,⁸ and investigate its motion in the x direction (i.e. under an additional potential $-eFx$) by the method introduced by Dirac.⁹ In place of equation (1), which was independent of time, we now have the relation

$$\Delta\psi - \mu(V - eFx)\psi + \frac{4\pi im}{h} \frac{\partial\psi}{\partial t} = 0. \quad (27)$$

To solve this we may assume a relation

$$\psi = \sum_{klm} c_{klm}(t) \cdot \psi_{klm} \cdot e^{-\frac{2\pi i}{h} E_{klm} t}.$$

Since (27) must be satisfied by $F = 0$ and $\frac{dc_{klm}}{dt} = 0$, we have

$$\frac{4\pi im}{h} \sum_{klm} \dot{c}_{klm}(t) \psi_{klm} e^{-\frac{2\pi i}{h} E_{klm} t} = -\frac{8\pi^2 m}{h^2} \cdot eFx\psi(t),$$

and hence at the time $t = 0$

$$\frac{4\pi im}{h} \sum_{klm} \dot{c}_{klm}(0) \psi_{klm} = -\frac{8\pi^2 m}{h^2} eFx\psi(0). \quad (28)$$

or, if the right-hand side is developed according to the proper functions of equation (1)

$$\dot{c}_{klm}(0) = \frac{2\pi i}{h} eF \int x\psi(0) \psi_{klm} dx dy dz \quad (29)$$

where the integration covers the whole fundamental paral-

This relation corresponds exactly with that used by Lorentz and Sommerfeld except that $\xi\eta\zeta$ are in general not the simple velocity components, but are other quantities connected with the velocities and also characterizing the quantum states.

§ 4. The Interactions between the Electrons and the Elastic Waves of the Lattice

We have already shown that as long as the lattice is strictly periodic, a definite momentum in the x , y , and z directions belongs to each state k , l , m , and the electrons can pass unimpeded through the lattice. To account for the appearance of a resistance which increases with the temperature we have to consider the influence of the thermal vibrations of the atoms, and we have in effect a disturbance problem of the interaction of the two coupled systems, the electron gas on the one hand, and the atomic lattice with its elastic vibrations on the other. The problem is naturally of a highly complex nature, and we shall therefore only indicate the line of approach adopted, and, for the details, reference must be made to the original paper.

At low temperatures we may assume that the elastic waves are long compared with the inter-atomic distances, and consider the crystal as continuous in respect to them, and we may further assume that the amplitudes are so small that the vibrations can be considered as harmonic.

As explained previously, the elastic displacement vector $u(xyz)$ will have the same periodicity as the proper functions of the electrons. If we write this in the form of a Fourier series

$$u = \sum_{fgh=-\infty}^{+\infty} \sum_{j=1}^3 \left[a_{fghj} \cos 2\pi \left(\frac{fx}{K} + \frac{gy}{L} + \frac{hz}{M} \right) + b_{fghj} \sin 2\pi \left(\frac{fx}{K} + \frac{gy}{L} + \frac{hz}{M} \right) \right] u_{fghj}, \quad (36)$$

it is, in the case of long waves, equivalent to describing the oscillations of the lattice by means of normal co-ordinates a_{fghj} , b_{fghj} , where the numbers fgh characterize the vector of spreading, and j the state of polarization of the normal oscillation considered. Also

$$a_{fghj} = a_{-f, -g, -h, j}; \quad b_{fghj} = -b_{-f, -g, -h, j}.$$

u_{fghj} is a unit vector in the direction of oscillation, and for $j = 1$ (longitudinal wave) it is parallel to fgh , and for $j = 2, 3$ (trans-

verse wave) it is perpendicular. In classical mechanics the normal co-ordinates satisfy the differential equations

$$\left. \begin{aligned} \ddot{a}_{fghj} + 4\pi^2 \nu_{fghj}^2 a_{fghj} &= 0 \\ \ddot{b}_{fghj} + 4\pi^2 \nu_{fghj}^2 b_{fghj} &= 0 \end{aligned} \right\} \quad . \quad . \quad . \quad (37)$$

where ν is the frequency, and

$$\nu_{fghj} = v_j \sqrt{\left(\frac{f}{K}\right)^2 + \left(\frac{g}{L}\right)^2 + \left(\frac{h}{M}\right)^2}, \quad . \quad . \quad . \quad (38)$$

v_1 being the velocity of transmission of longitudinal, and $v_2 = v_3$ that of transverse waves.

In quantum mechanics the exact function $a_{fghj}(t)$ cannot be obtained, and we have instead, according to Schrödinger,¹⁰ the amplitude of probability $\psi(a_{fghj})$ satisfying the equation

$$\frac{d^2\psi}{da_{fghj}^2} + \frac{8\pi^2 M}{h^2} (E - 2\pi^2 M \nu_{fghj}^2 a_{fghj}^2) \psi = 0. \quad . \quad . \quad (39)$$

Here M is the mass of the oscillator (which in our case is that of the fundamental parallelepiped), and E the energy of the proper vibration $fghj$. The value of E corresponding to the proper function $\psi_{q(fghj)}(a_{fghj})$ is

$$E_{q(fghj)} = [q(fghj) + \frac{1}{2}] h \nu_{fghj}. \quad . \quad . \quad . \quad (40)$$

The corresponding expression for $b_{fghj}(t)$ is

$$E_{r(fghj)} = [r(fghj) + \frac{1}{2}] h \nu_{fghj}, \quad . \quad . \quad . \quad (40a)$$

where $q(fghj)$ and $r(fghj)$ are the quantum numbers of the two vibrations characterized by $fghj$.

As long as we ignore all interaction between the electrons and the atoms, each electron state klm will have energy E_{klm} given by the previous equations (page 349), and the energy of the lattice will be given by (40). In this case the proper functions and energies of the system considered as a whole are given by

$$\psi_{klm, q(fghj), r(fghj)} = \psi_{klm} \prod_{fghj} \psi_{q(fghj)} \psi_{r(fghj)} \cdot e^{\frac{2\pi i}{h} E_{klm, q(fghj), r(fghj)}}. \quad (41)$$

$$\text{and} \quad E_{klm, q(fghj), r(fghj)} = E_{klm} + \sum_{fghj} E_{q(fghj)} + E_{r(fghj)}. \quad . \quad . \quad (42)$$

But if the two systems are to be coupled, we shall have to add an energy of interaction W , in connexion with which we shall assume that as the result of the elastic displacement (36) the value of the electrostatic potential in which the electron moves

is as great at the point r as it would be at the point $r-u$ in the absence of the displacement, so that for the new potential $V^*(r)$

$$V^*(r) = V(r-u) = V(r) - W(r).$$

Since $|u|$ is small compared with the lattice constant, and hence with the distance in which an appreciable change in V takes place, we may put

$$W(r) = (\text{grad } V, u),$$

so that according to (36)

$$\left. \begin{aligned} W(xyz, a_{fghj}, b_{fghj}) = & \sum_{fgh=-\infty}^{+\infty} \sum_{j=1}^3 \left[a_{fghj} \cos 2\pi \left(\frac{fx}{K} + \frac{gy}{L} + \frac{hz}{M} \right) \right. \\ & \left. + b_{fghj} \sin 2\pi \left(\frac{fx}{K} + \frac{gy}{L} + \frac{hz}{M} \right) \right] (\text{grad } V, u_{fghj}). \end{aligned} \right\} \quad (43)$$

As before we solve the Schrödinger equation of the entire system disturbed by the additional energy (43) by Dirac's method of varying the constants, and in this case the analysis shows that if at time $t = 0$, the electron is in the condition $k'l'm'$, and the lattice in the state $q'(fghj)$, $r'(fghj)$, the probability that at time t , the whole system is in the state klm , $q(fghj)$ is given by

$$\left. \begin{aligned} |c_{klm, q(fghj)}|^2 = & 2 |J_{klm, k'l'm', j_1}|^2 \frac{h}{8\pi^2 M \nu (f_1 g_1 h_1 j_1)} \\ & \left\{ \begin{aligned} & \frac{1 - \cos \frac{2\pi t}{h} [E_{klm} - E_{k'l'm'} + h\nu (f_1 g_1 h_1 j_1)]}{[E_{klm} - E_{k'l'm'} + h\nu (f_1 g_1 h_1 j_1)]^2} (q(f_1 g_1 h_1 j_1) + 1) \\ & \frac{1 - \cos \frac{2\pi t}{h} [E_{klm} - E_{k'l'm'} - h\nu (f_1 g_1 h_1 j_1)]}{[E_{klm} - E_{k'l'm'} - h\nu (f_1 g_1 h_1 j_1)]^2} q(f_1 g_1 h_1 j_1). \end{aligned} \right\} \quad (44) \end{aligned}$$

where $J_{klm, k'l'm', j_1}$ is a coefficient of a term in a matrix element of the interaction energy W (equation (43)) between electron and lattice waves, corresponding to a transition of the electron from the state klm to the state $k'l'm'$, together with a loss or gain of one energy quantum by the lattice wave $f^*g^*h^*j^*$, all the other lattice waves retaining their previous energies. To obtain this matrix element it is necessary to multiply the interaction energy (43) by the wave-function of the initial state of the whole system, and by the conjugate complex of the wave function of the final state, and then to integrate over all co-ordinates involved, i.e. the three co-ordinates of the electron, and the amplitudes of all lattice waves. The initial wave function is a product of the func-

tion $\psi_{klm}(xyz)$ of the electron co-ordinates, and certain Hermitian functions $\psi(H)$ of the amplitudes of the lattice waves. The final wave function contains the same Hermitian function of all lattice wave amplitudes except $a_{f^*g^*h^*j^*}$, the function H_q (constant $a_{f^*g^*h^*j^*}$) being replaced by $H_{q\pm 1}$ (constant $a_{f^*g^*h^*j^*}$), and the function $\psi_{klm}(xyz)$ by $\psi_{k'l'm'}(xyz)$. On carrying out the first integration with respect to all the amplitudes a_{fghj} of the lattice waves, all terms in the summation of (43) cancel out except $a_{f^*g^*h^*j^*} \cos 2\pi \left(\frac{f^*x}{K} + \frac{g^*y}{L} + \frac{h^*z}{M} \right)$, this term giving the well known matrix element of the oscillator co-ordinate multiplied by the unaltered function $\cos 2\pi \left(\frac{f^*x}{K} + \frac{g^*y}{L} + \frac{h^*z}{M} \right)$, this function being independent of the amplitudes a_{fghj} of the lattice waves. There remains an integration over the co-ordinates of the electron, namely

$$\int \psi_{klm} \bar{\psi}_{k'l'm'} \cos 2\pi \left(\frac{f^*x}{K} + \frac{g^*y}{L} + \frac{h^*z}{M} \right) dx dy dz.$$

Taking over the factor $\text{grad}(V u_{f^*g^*h^*j^*})$ by which the term $a_{f^*g^*h^*j^*} \dots$ is multiplied in (43), and inserting the values of ψ required by (4), we obtain the expression $J_{klm, k'l'm', j^*}$ in (44), this expression being therefore what remains after carrying out the integration in (43) over all the $d a_{fghj}$. The analysis then indicates that the terms $J_{klm, k'l'm', j^*}$ are given by the relation

$$J_{klm, k'l'm', j^*} = \frac{1}{2} \int (\text{Grad } V u_{f^*g^*h^*j^*}) \overline{u_{k'l'm'}} dx dy dz. \quad (44a)$$

Exactly similar considerations hold if r changes instead of q . If one integrates over a small energy interval and differentiates with regard to the time, the right-hand side of this expression gives the probability of a transition from the 'dashed' to the 'undashed' state, and hence the c_{klm} will increase when the denominators in (44) are very small, or in other words to an approximation if

$$E_{klm} - E_{k'l'm'} = \pm h\nu(f_1 g_1 h_1 j_1). \quad (44b)$$

Hence, just as in the later developments of the Houston theory, the conclusion is that the essential scattering processes are not elastic collisions, but always involve an interchange of energy $h\nu$ between the lattice and the electron.

Further treatment of the problem in this way leads to very great difficulties, and we may therefore make the following simplifying assumptions in order to show that the general principles used lead to results of the right order of magnitude.

We may choose our crystal so that $G_1 = G_2 = G_3 = G$ } (45a)
and let $a = b = c$

We may assume that the electron gas is completely degenerate so that $T \ll T_0$ (45b)

and let the energy be given by

$$E_{klm} = \omega \left[\left(\frac{2\pi k}{G} \right)^2 + \left(\frac{2\pi l}{G} \right)^2 + \left(\frac{2\pi m}{G} \right)^2 \right] \quad . \quad . \quad (45c)$$

and let the momentum in the x direction be

$$\tau \frac{2\pi k}{G} \quad . \quad . \quad . \quad . \quad . \quad . \quad (45d)$$

and the velocity of transmission of longitudinal and transverse waves

$$v_1 = v_2 = v_3 = v \quad . \quad . \quad . \quad . \quad (45e)$$

We may next consider the expression $|J_{klm, k'l'm', j}|^2$ in (44). If we use (44a), and write for abbreviation $(\text{grad } V, u_{fsg^*h^*j^*}) = \frac{\partial V}{\partial s}$ we have

$$2J_{klm, k'l'm', j} = \int \frac{\partial V}{\partial s} u_{klm} \overline{u_{k'l'm'}} dx dy dz.$$

Since the integrand is periodic we obtain on integration by parts

$$2J_{klm, k'l'm', j} = - \int V \frac{\partial}{\partial s} u_{klm} \overline{u_{k'l'm'}} dx dy dz \quad . \quad . \quad (46)$$

Introducing into (1) the expression given by (4a) for ψ_{klm} and putting \mathfrak{k} for the vector with components $k/K, l/L, m/M$ we obtain

$$\Delta u_{klm} + 2\pi i(\mathfrak{k}, \text{grad } u_{klm}) + \mu \left(E_{klm} - \frac{4\pi^2}{\mu} \mathfrak{k}^2 - V \right) u_{klm} = 0$$

$$\Delta \overline{u_{k'l'm'}} + 2\pi i(\mathfrak{k}', \text{grad } \overline{u_{k'l'm'}}) + \mu \left(E_{k'l'm'} - \frac{4\pi^2}{\mu} \mathfrak{k}'^2 - V \right) \overline{u_{k'l'm'}} = 0.$$

Multiplying the upper equation by $\frac{\partial \overline{u_{k'l'm'}}}{\partial s}$, and the lower by $\frac{\partial u_{klm}}{\partial s}$, and adding them together, we obtain on integration by parts

$$\begin{aligned} \mu \int V \frac{\partial}{\partial s} u_{klm} \overline{u_{k'l'm'}} dx dy dz &= 2\pi i \left(\mathfrak{k} - \mathfrak{k}', \int \text{grad } u_{klm} \frac{\partial \overline{u_{k'l'm'}}}{\partial s} dx dy dz \right) \\ &+ \mu \left[E_{klm} - E_{k'l'm'} - \frac{4\pi^2}{\mu} (\mathfrak{k}^2 - \mathfrak{k}'^2) \right] \cdot \int u_{klm} \frac{\partial \overline{u_{k'l'm'}}}{\partial s} dx dy dz. \quad (47) \end{aligned}$$

which vanishes for $k = k', l = l', m = m'$.

From (45c) the second term on the right-hand side may be neglected compared with the first, because we are only concerned with transitions in which the energy of an electron undergoes but small changes. As regards the first term we shall assume as in (2) that the function u_{klm} for the elementary parallelepiped can be written in the form

$$u_{klm} = \varphi,$$

where φ , the proper function of the isolated atom, is considered as spherically symmetrical. If we then write for

$$\int \left(\frac{\partial \varphi}{\partial x} \right)^2 dx dy dz = \int \left(\frac{\partial \varphi}{\partial y} \right)^2 dx dy dz = \int \left(\frac{\partial \varphi}{\partial z} \right)^2 dx dy dz = C. \quad (48)$$

we have

$$J_{klm, k'l'm', 1} = -\frac{\pi i}{\mu} |\mathbf{r} - \mathbf{r}'| \cdot C \quad . \quad . \quad . \quad (49)$$

for the case of longitudinal waves, whilst for transverse waves

$$J_{klm, k'l'm', 2, 3} = 0.$$

We have now to calculate the number of electrons moving out of the state klm in unit time owing to interaction with the lattice, and since there is to be statistical equilibrium this must be equal to the number entering the state klm owing to the acceleration produced by the external field. When no external field is present it can be shown that equilibrium exists if the electrons are distributed according to Fermi's function

$$f_0(E_{klm}) = \frac{1}{\frac{1}{A} e^{\frac{E_{klm}}{kT}} + 1} \quad . \quad . \quad . \quad (50)$$

and the probability of the oscillators considered as an undegenerate system is given by the classical formula

$$g(q_{gh}h_j) = \text{const } e^{-\frac{E_{qghj}}{kT}} \quad . \quad . \quad . \quad (51)$$

As in the Lorentz and Sommerfeld theories we assume that the distribution in the presence of the field differs but slightly from f_0 , so that we may write

$$f(\xi\eta\zeta) = f_0(\xi\eta\zeta) + \xi\chi(\varrho), \quad . \quad . \quad . \quad (52)$$

where χ is a small function of $\varrho = \sqrt{\xi^2 + \eta^2 + \zeta^2}$. We now have to determine χ from the fact that a stationary state is to be set

up. To do this we require the number of electrons moving out of the state klm in unit time, their distribution function being given by (52). Here we shall only deal with the processes of interaction with the a -oscillators given by (44), since the calculation for the b -oscillator is identical.

Suppose now that $B_{k'l'm'q}^{klmq}(f^*g^*h^*j^*)$ is the probability of an electron transition from klm to $k'l'm'$, in the course of which an oscillator characterized by

$$f^* = \pm(k-k'), g^* = \pm(l-l'), h^* = \pm(m-m'). \quad (53)$$

moves from $q(f^*g^*h^*j^*)$ to $q'(f^*g^*h^*j^*)$. Then the total number of electrons leaving klm in unit time is given by

$$\sum_{k'l'm'q'} \sum_q B_{k'l'm'q'}^{klmq} g(q) \cdot f(klm) [1 - f(k'l'm')],$$

and the number entering the state klm by

$$\sum_{k'l'm'q'} \sum_q B_{klmq}^{k'l'm'q'} g(q') f(k'l'm') [1 - f(klm)]$$

and the difference of these two expressions, using the relation $B_{k'l'm'q'}^{klmq} = B_{klmq}^{k'l'm'q'}$, is

$$n_a = \sum_{k'l'm'q'} \sum_q B_{k'l'm'q'}^{klmq} \{g(q)f(klm)[1 - f(k'l'm')] - g(q')f(k'l'm')[1 - f(klm)]\}. \quad (54)$$

According to (51) and (40)

$$g(q_{fghj}) = \text{const } e^{-\frac{(q_{fghj} + \frac{1}{2})h\nu_{fghj}}{kT}},$$

and since $\sum_{q=0}^{\infty} g(q)$ must equal unity, it follows that

$$g(q_{fghj}) = e^{-\frac{q_{fghj} \cdot h\nu_{fghj}}{kT}} \left(1 - e^{-\frac{h\nu_{fghj}}{kT}}\right) \quad (55)$$

The probabilities of transition $B_{k'l'm'q'}^{klmq}$ are given by (44). In addition to the abbreviations previously used we may now write

$$\frac{2\pi(k-k')}{G} = X, \frac{2\pi(l-l')}{G} = Y, \frac{2\pi(m-m')}{G} = Z, \quad (56a)$$

$$\sqrt{\xi^2 + \eta^2 + \zeta^2} = \varrho, \sqrt{\xi'^2 + \eta'^2 + \zeta'^2} = \varrho', \sqrt{X^2 + Y^2 + Z^2} = R \quad (56b)$$

$$\frac{1}{x^2} \left(1 - \cos \frac{2\pi t}{h}\right) = \Omega(x) \quad (56c)$$

To obtain n_a we may introduce XYZ as variables in place of

$\xi'\eta'\zeta'$, and use polar co-ordinates R, ϑ, φ in the XYZ space, so that instead of R in (56b) we have what is proportional to it from (38)

$$\nu(XYZj^*) = \frac{v_{j^*}}{2\pi a} R,$$

in which case the analysis indicates that

$$n_a = \frac{(aG)^3}{M} \frac{2\pi C^2}{8\varrho a \omega v^4 \mu^2} \iint \frac{\nu^2 dv d\varphi}{e^{\frac{h\nu}{kT}} - 1} \left\{ \xi \chi(E) \frac{f_0(E+h\nu) \cdot e^{\frac{h\nu}{kT}} + f_0(E-h\nu)}{f_0(E)} \right. \\ \left. - \xi' \left[\chi(E+h\nu) \frac{f_0(E)}{f_0(E+h\nu)} + \chi(E-h\nu) \frac{f_0(E)}{f_0(E-h\nu)} \cdot e^{\frac{h\nu}{kT}} \right] \right\}. \quad (57)$$

Since statistical equilibrium is to exist in the presence of a field we have from (35), and (56b)

$$n_a = -\frac{2\pi e F a}{h} \frac{\partial f_0}{\partial \xi} = -\frac{2\pi e F a}{h} \frac{\partial f_0}{\partial \varrho} \frac{\xi}{\varrho}. \quad (58)$$

As in the theory of specific heats we may break off the elastic spectrum at a limiting value ν_0 , which is given by $\frac{h\nu_0}{k\Theta_0} = 1$, where Θ_0 is the characteristic temperature, and we may use a new integration variable $x = \frac{h\nu}{kT}$.

If the electron gas is completely degenerate we have in (50)

$$A = e^{\frac{\omega \varrho_0^2}{kT}},$$

writing $\varrho_0 = \sqrt[3]{6\pi^2 \kappa}$ as on page 351, and $\omega \varrho_0^2$ is the energy in the region where the value of $f_0(E)$ falls off sharply in the Fermi-Dirac distribution curve. If we introduce in place of E , the dimensionless expression

$$\epsilon = \frac{E - \omega \varrho_0^2}{kT} \quad (59)$$

we obtain

$$f_0(E) = f_0(\epsilon) = \frac{1}{e^\epsilon + 1} \quad (59a)$$

and

$$-\frac{\partial f_0}{\partial E} = -\frac{1}{kT} \frac{df_0}{d\epsilon} = \frac{1}{kT} \frac{1}{(e^\epsilon + 1)(e^{-\epsilon} + 1)} \quad (59b)$$

will differ appreciably from zero only in the region $\epsilon = 0$. In place of the function $\chi(E) = \chi(\epsilon)$ we may now introduce a new function,

$$c(\epsilon) = kT(e^\epsilon + 1)(e^{-\epsilon} + 1)\chi(\epsilon) = \frac{\chi(E)}{-\frac{\partial f_0}{\partial E}} \quad (60)$$

and use the abbreviations

$$P = \frac{eFa}{h} \frac{M}{G^3} \frac{16a\omega^2\varrho_0 v \mu^2}{2\pi C^2} \left(\frac{h\nu}{ak\Theta_0} \right)^3; \quad Q = \frac{4\pi^2}{2\varrho_0^2} \left(\frac{ak\Theta_0}{h\nu} \right)^2, \quad (61)$$

we obtain from (57), (58), and 59(a) the relation

$$\int_0^{\Theta_0/T} \left\{ \frac{e^\epsilon + 1}{e^\epsilon + e^{-x}} \left[c(\epsilon) - \left(1 - Q \left(\frac{T}{\Theta_0} \right)^2 x^2 \right) c(\epsilon + x) \right] \right. \\ \left. + \frac{e^{-\epsilon} + 1}{e^{-\epsilon} + e^{-x}} \left[c(\epsilon) - \left(1 - Q \left(\frac{T}{\Theta_0} \right)^2 x^2 \right) c(\epsilon - x) \right] \right\} \frac{x^2 dx}{e^x - 1} = P \left(\frac{\Theta_0}{T} \right)^3. \quad (62)$$

Since the electron cannot give off more energy than its initial content E , the integration in the last term should strictly speaking be extended only to the point $kTx = E$, but it can be shown that the value of the function $c(\epsilon)$ only concerns us in the region of the critical place at which the Fermi-Dirac distribution curve bends sharply, where $E = \omega\varrho_0^2$, and since $k\Theta < \varrho_0^2$ the limit $\frac{\Theta_0}{T}$ can be considered valid.

We may now see what these expressions indicate as regards the effect of temperature upon conductivity, and as before we may deal with the two cases $T \gg \Theta_0$, and $T \ll \Theta_0$.

1. $T \gg \Theta_0$.

Here we expect the same result for $\chi(E)$ as in the theory of Lorentz, namely

$$\chi(E) = -c \frac{\partial f_0}{\partial E},$$

whereby from (59b) and (60)

$$c(\epsilon) = c = \text{constant}.$$

The difference between the present calculations and those based on the classical theory lies in the use of the Pauli restriction principle in connexion with the collisions. This can be seen in the case of the expression within the bracket in (54) which from the classical point of view would be

$$g(q)[f(klm) - f(k'l'm')].$$

But for $T \gg \Theta_0$ all the proper oscillations are strongly excited so that their quantum numbers are much greater than unity, so that we may write $q' = q \pm 1 = q$, and if in (54) we write

$$g(q) = g(q'),$$

we obtain the classical value.

The assumption $c(\epsilon) = c$ does satisfy (62) since $\frac{\Theta_0}{T} \ll 1$, and

hence $x \ll 1$, and so we may write

$$Q\left(\frac{T}{\Theta_0}\right)^2 \int_0^{\Theta_0/T} \left\{ \frac{e^\epsilon + 1}{e^\epsilon + e^{-x}} c(\epsilon + x) + \frac{e^{-\epsilon} + 1}{e^{-\epsilon} + e^{-x}} c(\epsilon - x) \right\} \frac{x^4 dx}{e^x - 1} \\ = 2cQ\left(\frac{T}{\Theta_0}\right)^2 \int_0^{\Theta_0/T} x^3 dx = \frac{c}{2} Q\left(\frac{\Theta_0}{T}\right)^2 = P\left(\frac{\Theta_0}{T}\right)^3.$$

And from (60) we obtain

$$\chi(\varrho) = -\frac{4FeMa^2\varrho^2\omega v\mu^2}{G^3\pi^3C^2h} \left(\frac{hv}{ak\Theta_0}\right)^5 \frac{\partial f_0}{\partial \varrho} \frac{\Theta_0}{T}. \quad (63)$$

Since from (45d) the momentum in the x direction corresponding to the state $\xi\eta\zeta$ is $\tau\xi$, the current flowing under the stationary distribution given by (52) is

$$J = \frac{2e}{mV} \iiint \tau\xi^2 \chi(\varrho) \frac{G^3}{8\pi^3} d\xi d\eta d\zeta \quad (64)$$

because the current due to $f_0(\xi\eta\zeta)$ vanishes, and the factor 2 is introduced in (64) to take into account the fact that the statistical weight of each state must be doubled on account of the spin, V being the volume of the crystal. By using the same methods as Lorentz and Sommerfeld, the expression obtained for the specific conductivity is

$$\sigma = \frac{J}{F} = \frac{4(6\pi^2\kappa)^2}{3\pi^5} \cdot \frac{e^2 d\tau\omega v a^2 \mu^2}{mC^2 h} \left(\frac{hv}{ak\Theta_0}\right)^5 \frac{\Theta_0}{T}, \quad (65)$$

where $d = \frac{M}{V}$ is the density.

In this expression, as in § 1b, ω is an energy of the order $\beta' \cdot 10^{-12}$ ergs. τ/m is of the order of the maximum velocity of the electrons, as can be seen from (45d) since k covers all values from $-G$ to $+G$. In the Sommerfeld theory this velocity is of the order 10^8 cm./sec., and we may thus put $\frac{\tau}{m} = \tau' \cdot 10^8$ cm./sec., so that for free electrons τ' and β' are of the order unity, and in order to give the effect of the binding we may assume $\tau' = \beta' = \frac{1}{10}$. From (48) C is the reciprocal square of a length of the order of the atomic radius (10^{-8} cm.). $\frac{hv}{ak\Theta_0}$ is a dimensionless number of the order unity. If we assume the temperature to be $T = 3\Theta_0$ we then find that σ is of the order 10^{18} es.u., which is the right order of magnitude. Further the resistance $W = \frac{1}{\sigma}$ is directly proportional to the absolute temperature in agreement with fact.

2. $T \ll \Theta_0$.

In this case the relation between temperature and resistance is quite different, and at first sight it may appear that the zero point energy of the lattice must give rise to a considerable resistance at the absolute zero. As we have already explained in connexion with the Houston theory, the solution of this difficulty lies in the fact that the electrons are assumed to be in thermal equilibrium, and to obey the restrictions of the Fermi-Dirac statistics. In contrast to the scattering of a beam of X-rays, an electron can therefore only give up energy to the lattice if there is a vacant state into which it can fall, and this becomes continually less possible as the absolute zero is approached. The conclusion that the collisions always involve an interchange of energy equal to $h\nu$ is thus of vital importance, since it is essential in order to account for the vanishing of the resistance at the absolute zero, and also, of course, accounts for the Joule heating effect.

In the first paper by Bloch only an approximate solution was given for low temperatures, and indicated a resistance varying as T^3 , but in a second paper¹¹ the problem has been investigated, and a resistance varying as T^5 has been deduced. As we have explained above, at low temperatures, the probability of electron scattering is diminished, and the scattering itself is appreciable only in the case of interactions in which the momentum of the electron is but slightly altered. We cannot, however, ignore the change in momentum in the x direction entirely, because if we do this and put ξ instead of ξ' , we find that in equation (62) the terms involving $\left(\frac{T}{\Theta_0}\right)^2$ fall out, and no steady state can exist in the presence of an external field.

We may therefore write $\xi' = \xi + X$, in which case if the steady state is represented by $f = f_0(E) + \xi\chi(E)$, the function χ is given by

$$\begin{aligned}
 c_1 \left(\frac{T}{\Theta_0}\right) \int_{x=0}^{\Theta_0/T} \int_{\varphi=0}^{2\pi} \frac{x^2 dx d\varphi}{e^x - 1} \xi \left\{ \chi(E) \frac{f_0(E + kTx)e^x + f_0(E - kTx)}{f_0(E)} \right. \\
 \left. - \chi(E + kTx) \frac{f_0(E)}{f_0(E + kTx)} - \chi(E - kTx) \frac{f_0(E)e^x}{f_0(E - kTx)} \right\} \\
 = -c_2 F \xi \frac{\partial f_0}{\partial Q} - c_1 \left(\frac{T}{\Theta_0}\right)^3 \int_{x=0}^{\Theta_0/T} \int_{\varphi=0}^{2\pi} \frac{x^2 dx d\varphi}{e^x - 1} X \left\{ \chi(E + kTx) \frac{f_0 E}{f_0(E + kTx)} \right. \\
 \left. + \chi(E - kTx) \frac{f_0(E)e^x}{f_0(E - kTx)} \right\}. \quad (66)
 \end{aligned}$$

If one puts the right-hand side of (66) equal to zero, the homogeneous equation has the solution $\chi_1(E) = \alpha \frac{df_0}{dE}$ where α is a constant. This implies that in the absence of an external disturbance, and as long as we consider only processes in which ξ does not change, then not only $f_0(E)$ but also

$$f = f_0(E) + \xi \chi_1(E) = f_0(E) + \alpha \xi \frac{df_0}{dE} \cong f_0(E + \alpha \xi)$$

describes a stationary distribution, since for states with equal ξ , between which interchange occurs, this is limited only by a constant additional term $\alpha \xi$ to the energy.

As an approximate solution of (66) we now write

$$\chi = \chi_1 + \chi_2 = \alpha \frac{df_0}{dE} + \chi_2, \quad (67)$$

and it can be shown that the constant α is such that $\chi_2 \ll \chi_1$, so that to a first approximation the term χ_2 can be neglected. In this case for $T \ll \Theta$, the solution is

$$\alpha = - \frac{P}{2Q} \left(\frac{\Theta_0}{T} \right)^5 \frac{1}{\Gamma(6) \sum_{n=1}^{\infty} \frac{1}{n^5}} \cong - \frac{P}{250Q} \left(\frac{\Theta_0}{T} \right)^5, \quad (68)$$

and the expression for the distribution function for $T \ll \Theta_0$ becomes

$$f = f_0 - \xi \frac{P}{250Q} \left(\frac{\Theta_0}{T} \right)^5 \frac{df_0}{dE}, \quad (69)$$

and the corresponding expression for the conductivity is

$$\sigma = \frac{J}{F} \frac{(6\pi^2 \kappa)^2}{360\pi s} \cdot \frac{e^2 d\tau \omega v a^2 \mu^2}{mc^2 \hbar} \left(\frac{h\nu}{ak\Theta_0} \right)^5 \left(\frac{\Theta_0}{T} \right)^5. \quad (70)$$

This requires the resistance at low temperatures to vary as T^5 , in contrast to the Grüneisen law which requires a variation as T^4 , but as we have already seen in connexion with the Houston theory, the T^5 is at any rate approximately true. The detailed examination of the factors affecting the function $\chi = \chi_1 + \chi_2$ show that it must vanish exponentially for $|\epsilon| \gg 1$, so that at low temperatures, as in the Sommerfeld and Houston theories, it is only the electrons with velocities near the critical point on the Fermi-Dirac distribution curve which are concerned in the conductivity process.

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